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JOURNAL AND PROCEEDINGS

OF THE

ROYAL SOCIETY

OF NEW SOUTH WALES

FOR

1941

(INCORPORATED 1881)

VOLUME LXXV

Parts I-IV

EDITED BY

THE HONORARY SECRETARIES

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN

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CONTENTS.

VOLUME LXXV

Part I*

Page.

ART. I.—Presidential Address. By A. P. Elkin, M.A., Ph.D. (Issued July 4, 1941) .. 1

ART. II.—The Effect of the Synthetic Œstrogens, Stilbœstrol and Hexœstrol on the Pouch and Scrotum of *Trichosurus vulpecula*. By A. Bolliger, Ph.D., and A. J. Canny, M.B., B.S. (Issued July 4, 1941) 21

ART. III.—Magnetic Studies of Coordination Compounds. Part V. Binuclear Copper Derivatives of Diphenyl Methyl Arsine. By D. P. Mellor, M.Sc., and D. P. Craig, B.Sc. (Issued July 4, 1941) 27

ART. IV.—Progressive Rates of Tax in Australia. By H. S. Carslaw, Sc.D., LL.D. (Issued August 18, 1941) 31

Part II†

ART. V.—Clarke Memorial Lecture. The Climate of Australia in Past Ages. By C. A. Sussmilch, F.G.S. (Issued September 11, 1941) 47

ART. VI.—An Examination of the Essential Oils Distilled from the Tips and Normal Cut of *Eucalyptus polybractea*. By Philip A. Berry, M.Sc., and Thomas B. Swanson, M.Sc. (Issued September 11, 1941) 65

ART. VII.—The Jurassic Fishes of New South Wales. By R. T. Wade, M.A., Ph.D. (Issued September 11, 1941) 71

ART. VIII.—Remarks on Goodness of Fit of Hypotheses and on Pearson's χ Test. By D. T. Sawkins, M.A. (Issued September 11, 1941) 85

Part III‡

ART. IX.—Permian Blastoids from New South Wales. By Ida A. Brown, D.Sc. (Issued October 27, 1941) 96

ART. X.—Bryozoa from the Silurian and Devonian of New South Wales. By Joan Crockford, B.Sc. (Issued November 27, 1941) 104

ART. XI.—A Note on Determinations of Physiological Specialisation in Flax Rust. By W. L. Waterhouse, M.C., D.Sc.Agr., D.I.C., and I. A. Watson, B.Sc.Agr., Ph.D. (Issued November 27, 1941) 115

ART. XII.—The Thiamin (Vitamin B_1) Content of the Urine of *Trichosurus vulpecula*. By A. Bolliger, Ph.D., and C. R. Austin, M.Sc., B.V.Sc. (Issued November 27, 1941) 118

ART. XIII.—The Chemistry of Bivalent and Trivalent Rhodium. Part I. A Qualitative Study of Trivalent Rhodium Salts; and the Properties of Some Rhodous Salts. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued January 9, 1942) 122

ART. XIV.—The Chemistry of Bivalent and Trivalent Rhodium. Part II. Hexacovalent Complexes of Rhodous Halides with Diphenylmethylarsine. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued January 9, 1942) 127

---

* Published August 27, 1941.

† Published September 23, 1941.

‡ Published March 17, 1942.

MAR - 3 1943

Part IV*

Page.

ART. XV.—Radial Heat Flow in Circular Cylinders with a General Boundary Condition. II. By J. C. Jaeger, M.A., D.Sc. (Issued April 22, 1942) 130

ART. XVI.—The Chemistry of Bivalent and Trivalent Rhodium. Part III. Compounds of Rhodic Halides with Tertiary Arsines. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued April 21, 1942) 140

ART. XVII.—The Triassic Fishes of New South Wales. By R. T. Wade, M.A., Ph.D. (Issued April 22, 1942) 144

ART. XVIII.—Studies on the Cultivation of the Tung Oil Tree, *Aleurites fordii*. Part II. Study of a Heavy Yield of Fruit Obtained on the North Coast of New South Wales. By A. R. Penfold, F.A.C.I., F.C.S., F. R. Morrison, A.S.T.C., A.A.C.I., and S. Smith-White, B.Sc.Agr. (Issued April 22, 1942) 148

ART. XIX.—The Stereochemistry of Some Metallic Complexes, with Special Reference to their Magnetic Properties and the Cotton Effect. By D. P. Mellor, M.Sc. (Issued April 21, 1942) 157

ART. XX.—On the Frequency of the Primes. By F. A. Behrend. (Issued May 15, 1942) 169

TITLE PAGE, CONTENTS, NOTICES, PUBLICATIONS i

OFFICERS FOR 1941-42 vii

LIST OF MEMBERS, AWARDS OF MEDALS, ETC. ix

ABSTRACT OF PROCEEDINGS xxi

PROCEEDINGS OF THE SECTION OF GEOLOGY xxx

PROCEEDINGS OF THE SECTION OF INDUSTRY xxxi

INDEX TO VOLUME LXXV xxxiii

* Published July 3, 1942.

NOTICE.

The Royal Society of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Authors should submit their papers in typescript and in a condition ready for printing. All physico-chemical symbols and mathematical formulæ should be so clearly written that the compositor should find no difficulty in reading the manuscript. Sectional headings and tabular matter should not be underlined. Pen-illustrations accompanying papers should be made with black Indian ink upon smooth white Bristol board. Lettering and numbers should be such that, when the illustration or graph is reduced to 5 inches in width, the lettering will be quite legible. On graphs and text figures any lettering may be lightly inserted in pencil. Photo-micrographs should be rectangular rather than circular, to obviate too great a reduction. The size of a full page plate in the Journal is $5 \times 7\frac{3}{4}$ inches, and the general reduction of illustrations to this limit should be considered by authors. When drawings, etc., are submitted in a state unsuitable for reproduction, the cost of the preparation of such drawings for the process-block maker must be borne by the author. The cost of colouring plates or maps must also be borne by the author. Further particulars regarding the preparation of manuscripts are contained in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

I bequeath the sum of £ to the Royal Society of New South Wales, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862–5, pp. 374, out of print.										
Vols.	I–XI	Transactions of the Royal Society, N.S.W.,					1867–1877			,,
Vol.	XII	Journal and Proceedings			,,	,,	1878,	pp.	324,	price 10s. 6d.
,,	XIII	,,	,,	,,	,,	,,	1879,	,,	255,	,,
,,	XIV	,,	,,	,,	,,	,,	1880,	,,	391,	,,
,,	XV	,,	,,	,,	,,	,,	1881,	,,	440,	,,
,,	XVI	,,	,,	,,	,,	,,	1882,	,,	327,	,,
,,	XVII	,,	,,	,,	,,	,,	1883,	,,	324,	,,
,,	XVIII	,,	,,	,,	,,	,,	1884,	,,	224,	,,
,,	XIX	,,	,,	,,	,,	,,	1885,	,,	240,	,,
,,	XX	,,	,,	,,	,,	,,	1886,	,,	396,	,,
,,	XXI	,,	,,	,,	,,	,,	1887,	,,	296,	,,
,,	XXII	,,	,,	,,	,,	,,	1888,	,,	390,	,,
,,	XXIII	,,	,,	,,	,,	,,	1889,	,,	534,	,,
,,	XXIV	,,	,,	,,	,,	,,	1890,	,,	290,	,,
,,	XXV	,,	,,	,,	,,	,,	1891,	,,	348,	,,
,,	XXVI	,,	,,	,,	,,	,,	1892,	,,	426,	,,
,,	XXVII	,,	,,	,,	,,	,,	1893,	,,	530,	,,
,,	XXVII	,,	,,	,,	,,	,,	1894,	,,	368,	,,
,,	XXIX	,,	,,	,,	,,	,,	1895,	,,	600,	,,
,,	XXX	,,	,,	,,	,,	,,	1896,	,,	568,	,,
,,	XXXI	,,	,,	,,	,,	,,	1897,	,,	626,	,,
,,	XXXII	,,	,,	,,	,,	,,	1898,	,,	476,	,,
,,	XXXIII	,,	,,	,,	,,	,,	1899,	,,	400,	,,
,,	XXXIV	,,	,,	,,	,,	,,	1900,	,,	484,	,,
,,	XXXV	,,	,,	,,	,,	,,	1901,	,,	581,	,,
,,	XXXVI	,,	,,	,,	,,	,,	1902,	,,	531,	,,
,,	XXXVII	,,	,,	,,	,,	,,	1903,	,,	663,	,,
,,	XXXVIII	,,	,,	,,	,,	,,	1904,	,,	604,	,,
,,	XXXIX	,,	,,	,,	,,	,,	1905,	,,	274,	,,
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,,	XLII	,,	,,	,,	,,	,,	1908,	,,	593,	,,
,,	XLIII	,,	,,	,,	,,	,,	1909,	,,	466,	,,
,,	XLIV	,,	,,	,,	,,	,,	1910,	,,	719,	,,
,,	XLV	,,	,,	,,	,,	,,	1911,	,,	611,	,,
,,	XLVI	,,	,,	,,	,,	,,	1912,	,,	275,	,,
,,	XLVII	,,	,,	,,	,,	,,	1913,	,,	318,	,,
,,	XLVIII	,,	,,	,,	,,	,,	1914,	,,	584,	,,
,,	XLIX	,,	,,	,,	,,	,,	1915,	,,	587,	,,
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,,	LI	,,	,,	,,	,,	,,	1917,	,,	786,	,,
,,	LII	,,	,,	,,	,,	,,	1918,	,,	624,	,,
,,	LIII	,,	,,	,,	,,	,,	1919,	,,	414,	,,
,,	LIV	,,	,,	,,	,,	,,	1920,	,,	312,	price £1 1s.
,,	LV	,,	,,	,,	,,	,,	1921,	,,	418,	,,
,,	LVI	,,	,,	,,	,,	,,	1922,	,,	372,	,,
,,	LVII	,,	,,	,,	,,	,,	1923,	,,	421,	,,
,,	LVIII	,,	,,	,,	,,	,,	1924,	,,	366,	,,
,,	LIX	,,	,,	,,	,,	,,	1925,	,,	468,	,,
,,	LX	,,	,,	,,	,,	,,	1926,	,,	470,	,,
,,	LXI	,,	,,	,,	,,	,,	1927,	,,	492,	,,
,,	LXII	,,	,,	,,	,,	,,	1928,	,,	458,	,,
,,	LXIII	,,	,,	,,	,,	,,	1929,	,,	263,	,,
,,	LXIV	,,	,,	,,	,,	,,	1930,	,,	434,	,,
,,	LXV	,,	,,	,,	,,	,,	1931,	,,	366,	,,
,,	LXVI	,,	,,	,,	,,	,,	1932,	,,	601,	,,
,,	LXVII	,,	,,	,,	,,	,,	1933,	,,	511,	,,
,,	LXVIII	,,	,,	,,	,,	,,	1934,	,,	328,	,,
,,	LXIX	,,	,,	,,	,,	,,	1935,	,,	288,	,,
,,	LXX	,,	,,	,,	,,	,,	1936,	,,	528,	,,
,,	LXXI	,,	,,	,,	,,	,,	1937,	,,	708,	,,
,,	LXXII	,,	,,	,,	,,	,,	1938,	,,	396,	,,
,,	LXXIII	,,	,,	,,	,,	,,	1939,	,,	344,	,,
,,	LXXIV	,,	,,	,,	,,	,,	1940,	,,	658,	,,
,,	LXXV	,,	,,	,,	,,	,,	1941,	,,	224,	,,

Royal Society of New South Wales

OFFICERS FOR 1941-1942

Patrons :

His Excellency the Governor-General of the Commonwealth of Australia,
The LORD GOWRIE, V.C., P.C., G.C.M.G., C.B., D.S.O.

His Excellency the Governor of New South Wales,
The LORD WAKEHURST, K.C.M.G.

President :

D. P. MELLOR, M.Sc.

Vice-Presidents :

H. S. HALCRO WARDLAW, D.Sc., F.A.C.I.
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Prof. T. G. ROOM, M.A.*
E. J. KENNY, M.Aust.I.M.M.

Honorary Secretaries :

Prof. A. P. ELKIN, M.A., Ph.D.
C. ANDERSON, M.A., D.Sc.

Honorary Treasurer :

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Members of Council :

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G. H. BRIGGS, D.Sc., Ph.D., F.Inst.P.
IDA A. BROWN, D.Sc.
W. R. BROWNE, D.Sc.
Prof. C. E. FAWSITT, D.Sc., Ph.D.
E. J. KENNY, M.Aust.I.M.M.
F. LIONS, B.Sc., Ph.D., A.I.C.†
W. H. MAZE, M.Sc.
G. D. OSBORNE, D.Sc., Ph.D.
A. CLUNIES ROSS, B.Sc., F.C.A. (*Aust.*).

* Resigned August 27, 1941.
† Elected September 18, 1941.

LIST OF THE MEMBERS

OF THE

Royal Society of New South Wales

as at March 1, 1942

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.		
1938	P 2	‡Albert, Adrien, Ph.D. *Lond.*, B.Sc. *Syd.*, A.I.C. *Gt. B.*, Commonwealth Research Fellow in Organic Chemistry, University of Sydney ; p.r. " Greenknowe," Greenknowe-avenue, Potts Point.
1935		‡Albert, Michel Francois, " Boomerang," Billyard-avenue, Elizabeth Bay.
1898		Alexander, Frank Lee, Surveyor, 21 George-street, Parramatta ; p.r. 154 William-street, Granville.
1941		Alldis, Victor le Roy, L.S., Registered Surveyor, Young, N.S.W.
1905	P 3	Anderson, Charles, M.A., D.Sc. *Edin.*, C.M.Z.S., 17 Towns-road, Vaucluse. (Hon. Secretary.) (President, 1924.)
1909	P 11	Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, " Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1930		Aston, Ronald Leslie, B.Sc., B.E. *Syd.*, M.Sc., Ph.D. *Cantab.*, A.M.I.E.Aust., Lecturer in Civil Engineering and Surveying in the University of Sydney ; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 1	Baker, Stanley Charles, M.Sc., F.Inst.P., Teacher of Physics, Newcastle Technical College, Islington ; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1939	P 1	Basnett, Elizabeth Marie, M.Sc., 36 Cambridge-street, Epping.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, " Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., c·o Tooth & Co. Limited, Sydney ; p.r. corner of The Crest and Rosebery-road, Killara.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., 15 Hilltop-road, Headington, Oxford, England.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney ; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale ; p.r. 17 Thompson-street, Clifton Gardens.
1939	P 2	Blake, George Gascoigne, M.I.E.E., F.Inst.P., " Holmleigh," Cecil-avenue, Pennant Hills.
1933	P 18	Bolliger, Adolph, Ph.D., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney.
1926	P 5	Booker, Frederick William, M.Sc., c/o Geological Survey, Mines Department, Sydney.
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., New England University College, Armidale. (Vice-President.) (President, 1935.)
1939		Bosworth, Richard Charles Leslie, M.Sc., D.Sc. *Adel.*, Ph.D. *Camb.*, F.A.C.I., F.Inst.P., c/o C.S.R. Co., Pyrmont ; p.r. 41 Spencer-road, Killara.
1922		Bradfield, John Job Crew, C.M.G., D.Sc. *Eng.*, M.E., M.Inst.C.E., M.Inst.E.Aust., Barrack House, 16 Barrack-street, Sydney ; p.r. 23 Park-avenue, Gordon

MAR - 3 1943

Elected.		
1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney; p.r. 28 Junction-road, Hornsby.
1940		Brigden, Alan Charles, B.Sc., 22 Kelso-street, Enfield.
1919	P 1	Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
1935	P 2	Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.
1941		Brown, Samuel Raymond, A.C.A. *Aust.*, 87 Ashley-street, Chatswood.
1913	P 21	Browne, William Rowan, D.Sc., Assistant-Professor of Geology in the University of Sydney. (Vice-President.) (President, 1932.)
1940		Buckley, Daphne M. (Mrs.), B.Sc., 4 Sharland-avenue, Chatswood.
1940		Buckley, Lindsay Arthur, B.Sc., 4 Sharland-avenue, Chatswood.
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. *Syd.*, F.R.A.C.S., "Radstoke," Elizabeth Bay.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1919	P 23	Burrows, George Joseph, B.Sc., Lecturer and Demonstrator in Chemistry in the University of Sydney.
1940		Cane, Reginald Frank, M.Sc., A.A.C.I., National Oil Pty. Ltd., Glen Davis, N.S.W.
1940		Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
1938	P 1	‡Carey, Samuel Warren, D.Sc., Practising Petroleum Geologist, c/o Australasian Petroleum Co., Port Moresby.
1903	P 4	Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
1913	P 4	Challinor, Richard Westman, F.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
1933		Chalmers, Robert Oliver, A.S.T.C., Assistant (Professional) in Mineralogy, Australian Museum, College-street, Sydney.
1940		Chambers, Maxwell Clark, B.Sc., c/o J. and E. Atkinson Pty. Ltd., 469-75 Kent-street, Sydney.
1913	P 19	Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
1935	P 2	Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
1935		Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
1940		Clarke, Ronald Stuart, B.A., 28 Beecroft-road, Beecroft.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
1941		Cohen, Max Charles, B.Sc., Box 2248 U, G.P.O., Melbourne.
1940		Cohen, Samuel Bernard, M.Sc., A.A.C.I., 9 Boonara-avenue, Bondi.
1940		Colditz, Margaret Joyce, B.Sc., 9 Beach-street, Kogarah.
1940		Cole, Edward Ritchie, B.Sc., 14 Barwon-road, Lane Cove.
1940	P 1	Cole, Joyce Marie, B.Sc., 14 Barwon-road, Lane Cove.
1940		Collett, Gordon, B.Sc., 49 Liverpool-road, Summer Hill.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1913	P 5	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1940		Cortis-Jones, Beverly, M.Sc., St. Andrew's College, Newtown.
1919		Cotton, Frank Stanley, D.Sc., Chief Lecturer and Demonstrator in Physiology in the University of Sydney.
1909	P 7	Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
1940		Cox, Morris Edward.
1941	P 1	Craig, David Parker, Research Scholar, 62 Springdale-road, Killara.
1921	P 1	‡Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street, Rockdale.
1940	P 3	Crockford, Joan Marian, B.Sc., 219 Victoria-road, Gladesville.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1940		Dadour, Anthony, 25 Elizabeth-street, Waterloo.
1890		Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.

Elected.		
1894		Dick, James Adam, C.M.G., B.A. *Syd.*, M.D., C.M. *Edin.*, F.R.C.S. *Edin.*, Col. A.A.M.C., Comr. Ord. St. John, Medical Practitioner, "Catfoss," 148 Belmore-road, Randwick.
1906		‡Dixson, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.I.C., F.A.C.I., 30 Hampden-road, Pennant Hills.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
1937	P 6	Dulhunty, John Allan, B.Sc., Geology Department, University of Sydney; p.r. 10 Tusculum-street, Potts Point.
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parrmaatta-road, Ashfield.
1934	P 16	Dwyer, Francis P. J., M.Sc., Lecturer in Chemistry, Technical College, Sydney.
1923	P 21	Earl, John Campbell, D.Sc., Ph.D., Professor of Organic Chemistry in the University of Sydney. (Vice-President.) (President, 1938.)
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.I.C., Professor in Engineering Technology and Metallurgy in the University of Sydney.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
1940		Emmerton, Henry James, B.Sc., 41 Nelson-street, Gordon.
1937		English, James Roland, L.S. A.I.F.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
1908		Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. *Lond.*, A.R.A.I.A., 6 Major-street, Coogee.
1921		Farnsworth, Henry Gordon, Government Stores, Harrington-street, Sydney; p.r. "Rothsay," 90 Alt-street, Ashfield.
1939		Faull, Norman Augustus, c/o National Standards Laboratory, University Grounds, Chippendale.
1909	P 7	Fawsitt, Charles Edward, D.Sc., Ph.D., Professor of Chemistry in the University of Sydney. (President, 1919.)
1923		Fiaschi, Piero, O.B.E., V.D., M.D. *Columbia Univ.*, D.D.S. *New York*, M.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 178 Phillip-street, Sydney.
1940		Finch, Franklin Charles, B.Sc.
1927	P 7	Finnemore, Horace, B.Sc., F.I.C., Reader in Pharmacy in the University of Sydney.
1935		Firth, Francis Williamson, Elliotts and Australian Drug Ltd., O'Connell-street, Sydney.
1935		Firth, John Clifford, B.Sc., "Avoca," Huntley's Point-road, Gladesville.
1940		Fisher, Robert, B.Sc., No. 4 Flat, 11 French-street, Maroubra.
1920		Fisk, Sir Ernest Thomas, K.B., F.Inst.R.E., A.M.I.E. *Aust.*, Chairman of Directors, Amalgamated Wireless (Australasia) Ltd., Wireless House, 47 York-street, Sydney; p.r. 16 Beaconsfield-parade, Lindfield.
1940		Flack, Arthur Charles Allenby, B.Sc., High School, Broken Hill.
1933		Fletcher, Harold Oswald, Assistant Palæontologist, Australian Museum, College-street, Sydney.
1879		‡Foreman, Joseph, M.R.C.S. *Eng.*, L.R.C.P. *Edin.*, "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c/o Westinghouse Sales & Rosebery, Dunning-avenue, Waterloo; p.r. Taren Point-road, Taren Point.
1905		Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1940		Freney, Martin Raphael, B.Sc., McMaster Laboratory, Sydney.
1935	P 2	Garretty, Michael Duhan, M.Sc., Chief Geologist, North Broken Hill Ltd., Broken Hill, N.S.W.
1939	P 2	Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
1940		Gillis, Richard Galvin, 27 Kia Ora, 453 St. Kilda-road, Melbourne, S.C.2.
1935		Goddard, Roy Hamilton, F.C.A. *Aust.*, Royal Exchange, Bridge-street, Sydney.

Elected.		
1936		Goulston, Edna Maude, B.Sc., Demonstrator in Micro-Chemistry in the University of Sydney; p.r. 83 Birriga-road, Bellevue Hill.
1940		Graves, John Nevil, B.Sc., 96 Wentworth-street, Randwick.
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney; p.r. 15A Wharf-road, Longueville.
1880	P 6	‡Halligan, Gerald Harnett, L.S., F.G.S., Retired Civil Engineer and Hydrographer, "The Straths," Pacific Highway, Killara.
1892		Halloran, Henry Ferdinand, L.S., 153 Elizabeth-street, Sydney.
1940		Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney; p.r. 4 Pearson-avenue, Gordon.
1905	P 6	Harker, George, D.Sc., F.A.C.I.; p.r. 75 Prospect-road, Summer Hill.
1936		Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., Physics Department, The University, Sydney.
1937	P 8	Harradence, Rita Harriet, M.Sc., Research Scholar, c/o Dyson Perrins Laboratory, Oxford University, Oxford, England.
1934		Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1923	P 3	Harrison, Travis Henry John, D.Sc.Agr., D.I.C. *London*, Commonwealth Fruit Officer, Australia House, Strand, London, England; p.r. 41 Queen's Gardens, Ealing, W.5, London.
1929		Hawley, J. William, J.P., Financial Agent, 4 Castlereagh-street, Sydney; p.r. 12 King's-road, Vaucluse.
1934		Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c/o Messrs. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 21 Wandella-avenue, Roseville.
1919		Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1940		Heselton, Thomas William, B.Sc., c/o Munition Laboratories, Maribyrnong, Victoria.
1935		Hewitt, Frank Rupert, 7 Tindale-road, Artarmon.
1938	P 2	Hill, Dorothy, M.Sc. *Q'ld.*, Ph.D. *Cantab.*, Geological Research Fellow, University of Queensland, Brisbane.
1918		Hindmarsh, Percival, M.A., B.Sc.Agr., Principal, Hurlstone Agricultural High School, Glenfield.
1936		Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
1928		Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (*Aust.*), A.M.Inst.T.; p.r. "St. Cloud," Beaconsfield-road, Chatswood.
1916		Hoggan, Henry James, A.M.I.M.E. *Lond.*, A.M.I.E. *Aust.*, Consulting and Designing Engineer, "Lincluden," 81 Frederick-street, Rockdale.
1930		Holmes, James Macdonald, Ph.D., F.R.G.S., F.R.S.G.S., Associate Professor of Geography in the University of Sydney.
1919		Hoskins, Arthur Sidney, Engineer, Steel Works, Port Kembla; postal address, P.O. Box 36, Wollongong.
1919		Hoskins, Cecil Harold, Engineer, c/o Australian Iron & Steel Ltd., Kembla Building, 58 Margaret-street, Sydney, Box 3375 R, G.P.O.
1941		Howard, Harold Theodore Clyde, B.Sc., Principal, Wollongong Technical High School, Wollongong.
1935		Howarth, Mark, Grange Mount, Bull-street, Mayfield, Newcastle, N.S.W.
1936		Howie, Sir Archibald, K.B., M.L.C., 7 Wynyard-street, Sydney.
1938	P 4	Hughes, Gordon Kingsley, B.Sc., Lecturer in Chemistry, University of Sydney.
1923	P 3	‡Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
1940		Johns, Thomas Harley, 130 Smith-street, Summer Hill.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1935	P 6	Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1911		Julius, Sir George A., Kt., B.Sc., B.E., M.I.Mech.E., M.I.E.Aust., Culwulla Chambers, Castlereagh-street, Sydney.

Elected.		
1935		Kelly, Caroline Tennant (Mrs.), "Eight Bells," Castle Hill.
1935		Kelly, Francis Angelo Timothy, "Eight Bells," Castle Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, c/o Australian Paper Mfrs. Ltd., Macauley-street, Matraville; p.r. 55 Harold-street, Matraville.
1896		King, Sir Kelso, K.B., Underwriter, 117 Pitt-street, Sydney.
1940		King, Leonard Esmond, 161 Nelson Bay-road, Bronte.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.
1939		Lambeth, Arthur James, "Yeronga," Wylde-street, Potts Point.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., P.O. Box. No. 21, Concord.
1924		Leech, Professor Thomas David James, B.Sc., B.E. *Syd.*, Professor of Engineering, Auckland University College, Auckland, N.Z.
1934		Leech, William Dale, Californian Institute of Technology, Pasadena, California, U.S.A.
1936	P 3	Lemberg, Max Rudolf, D.Phil., Biochemist, Royal North Shore Hospital; p.r. 12 de Villiers-avenue, Chatswood.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1940		Lincoln, Gordon James, 15 Turner-avenue, Haberfield.
1929	P 54	Lions, Francis, B.Sc., Ph.D., A.I.C., Department of Chemistry, University of Sydney; p.r. 31 Chesterfield-road, Epping.
1940		Lipson, Menzie, Chemist, C.S.I.R., 5 Phillip Court, Latimer-road, Rose Bay.
1940	P 1	Lockwood, William Hutton, B.Sc., Institute of Anatomy, Canberra, A.C.T.
1906		Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1927	P 1	Love, William Henry, B.Sc., Ph.D., Lecturer in Physics, University of Sydney.
1940		Luciano, Albert Anthony, 16 Arthur-street, Bellevue Hill.
1939	P 1	Maccoll, Allan, M.Sc., 76 Springdale-road, Killara.
1940		Maccoll, Mrs. Margaret Elphinstone, B.A., B.Ec., 76 Springdale-road, Killara.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2	McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	‡McKay, R. T., L.S., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1932		McKie, Rev. Ernest Norman, B.A. *Syd.*, St. Columba's Manse, Guyra.
1927		McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W.
1940		Malone, Edward E., 45 Norton-street, Randwick.
1924		Mance, Frederick Stapleton, "Binbah," Lucretia-avenue, Longueville.
1926		Mathews, Hamilton Bartlett, B.A., F.I.S., F.C.I.V., Box 2968 NN, G.P.O., Sydney.
1935		Maze, Wilson Harold, B.Sc., Lecturer in Geography, University of Sydney.
1941		Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1912		Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
1929	P 16	Mellor, David Paver, M.Sc., Lecturer and Demonstrator, Chemistry Department, University of Sydney; p.r. 35 Oliver-road, Roseville. (President.)
1940		Mercer, Edgar Howard, McMaster Laboratory, Parramatta-road, Glebe.
1928		Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood.
1940		Mills, James Edward, M.Sc., Ph.D., 16 Smith-road, Artarmon.
1940		Morris, Benjamin Sydney, 22 Kelso-street, Enfield.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P 25	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney.
1934		Mort, Francis George Arnot, Manufacturing Chemist, 16 Grafton-street, Woollahra.
1915		Murphy, Robert Kenneth, Dr.Ing., Chem.Eng., A.S.T.C., M.I.Chem.E., A.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.

Elected.		
1940		Murray, Alban James Moore, B.Sc., 54 Sydney-road, Willoughby.
1923	P 2	Murray, Jack Keith, B.A., B.Sc.Agr., Principal, Queensland Agricultural College, Gatton, Queensland, and Professor of Agriculture in the University of Queensland.
1930	P 6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., Assistant Director, Australian Institute of Industrial Psychology, 12 O'Connell-street, Sydney; p.r. "Kingsleigh," Ingleburn, N.S.W.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Biology, Victoria University College, Wellington, N.Z.
1935		Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
1938	P 1	Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., Secretary, Linnean Society of N.S.W., Science House, Gloucester-street, Sydney.
1920	P 4	‡Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (Vice-President.) (President, 1934.)
1940		Norrie, Jack Campbell, B.Sc., 28 Ray-road, Epping.
1940	P 3	Nyholm, Ronald Sydney, B.Sc., 77 Bland-street, Ashfield.
1935		O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
1903		‡Old, Richard, "Waverton," Bay-road, North Sydney.
1913		Ollé, A. D., F.C.S., A.A.C.I., "Kareema," Charlotte-street, Ashfield.
1921	P 5	Osborne, George Davenport, D.Sc., Ph.D. *Camb.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1928		Parsons, Stanley William Enos, Analyst and Inspector, N.S.W. Explosive Department; p.r. Shepherd-road, Artarmon.
1920	P 72	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo; p.r. 67 Park-avenue, Roseville. (Hon. Treasurer.) (President, 1935.)
1933		Penman, Arthur Percy, B.E. *Syd.*, Mining Engineer, 10 Water-street, Wahroonga.
1940		Pettingell, William Walter, B.Sc., 28 Conder-street, Burwood.
1938		Phillips, Marie Elizabeth, B.Sc., 20 Kardinia-road, Clifton Gardens.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliffe.
1938		Pickard, Una Annie Frazer, B.Sc., Microscopist, 5 Malvern-avenue, Croydon.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
1896		‡Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
1921	P 2	Powell, Charles Wilfrid Roberts, F.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1918		Powell, John, Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
1918		Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney.
1893		Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	‡Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
1940		Ralph, Colin Sydney, 87 Ballandella-road, Toongabbie West.
1922		Raggatt, Harold George, D.Sc., Geological Adviser to the Commonwealth of Australia, Census Building, Canberra, A.C.T.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.

Elected.		
1936		Randall, Harry, Buena Vista-avenue, Denistone.
1931	P 1	Rayner, Jack Maxwell, B.Sc., F.Inst.P., Physicist to the Department of Mines, Sydney; p.r. 125 William-street, Granville.
1935		Reid, Cicero Augustus, 19 Newton-road, Strathfield.
1932		Richardson, Henry Elmar, Chemist, Chase-road, Turramurra.
1939	P 5	Ritchie, Ernest, B.Sc., 6 Military-road, North Bondi.
1933		Roberts, Richard George Crafter, Electrical Engineer, "Lameroo," Church Point, N.S.W.
1940		Robertson, Rutherford Ness, B.Sc. *Syd.*, Ph.D. *Cantab.*, Flat 4, 43 Johnston-street, Annandale.
1935		Robinson, Albert Jordan, Managing Director, S. T. Leigh & Co. Ltd., Raleigh Park, Kensington.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
1928		Ross, Allan Clunies, B.Sc., F.C.A. *Aust.*, Chartered Accountant *Aust.*, 54A Pitt-street, Sydney; p.r. The Grove, Woollahra. (Member from 1915 to 1924.)
1940		Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
1929		Royle, Norman Dawson, M.D., Ch.M., 185 Macquarie-street, Sydney.
1940		Sarroff, Carlyle Joseph.
1935		Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
1941	P 1	Sawkins, Dansie Thomas, M.A. *Syd.*, B.A. *Camb.*, Reader in Statistics, The University, Sydney; p.r. 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.Sc. *Syd.*, A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1940		Scott, Reginald Henry, B.Sc., 154 Highfield-road, Camberwell, Vic.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, Sacred Heart College, Glenelg, S.A.
1936		Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. *Melb.*, 43 Robertson-road, Centennial Park.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1938		Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, 2 Edward-street, Gordon.
1900		‡Simpson, R. C., Lecturer in Electrical Engineering, Technical College, Sydney.
1933		Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Ltd., Manufacturing Chemists, 23 Rosebery-avenue, Rosebery; p.r. "Raiatea," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, 1 Rocklands-road, Wollstonecraft.
1922	P 1	Smith, Thomas Hodge, Australian Museum, College-street, Sydney.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboonoo," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1900	P 1	‡Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1909		Stokes, Edward Sutherland, M.B., Ch.M. *Syd.*, D.P.H. *Irel.*, Medical Officer, Metropolitan Board of Water Supply and Sewerage, 341 Pitt-street, Sydney; p.r. 15 Highfield-road, Lindfield.
1916	P 1	Stone, Walter George, F.S.T.C., A.A.C.I., Senior Analyst, Department of Mines, Sydney; p.r. 14 Rivers-street, Bellevue Hill.
1940		Stroud, Richard Harris, "Dalveen," corner Chalmers and Barker-roads, Strathfield.
1918		‡Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1901	P 16	‡Sussmilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (President, 1922.)
1919		‡Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor of Mechanical Engineering in the University of Sydney.

Elected.		
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*, Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney ; p.r. " Lynton," 27 Kent-road, Rose Bay.
1941		Suvoroff, Victoria, B.Sc., Chief Chemist and Metallurgist, c/o G. E. Crane & Sons, Pty., Burwood-road, Concord.
1941	P 1	Swanson, Thomas Baikie, M.Sc. *Adel.*, Lecturer in Chemistry, New England University College, Armidale.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney ; p.r. 44 Kenneth-street, Longueville.
1935		Tennant, Thomas Henry, Manager, Government Stores Department ; p.r. 2 Borrodale-road, South Kensington.
1939		Thomas, Mrs. A. V. M., 12 Clifton-avenue, Burwood.
1919		Thorne, Harold Henry, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S., Lecturer in Mathematics in the University of Sydney ; p.r. 55 Railway-crescent, Beecroft.
1923		Tindale, Harold, General Manager, The Australian Gas Light Company, Haymarket, Sydney.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., P.O. Box 97, Atherton, North Queensland.
1923		Toppin, Richmond Douglas, A.I.C., 231 Weston-road, Rozelle.
1940		Tow, Aubrey James, M.Sc., No. 5, " Werrington," Manion-avenue, Rose Bay.
1932	P 8	Trikojus, Victor Martin, B.Sc., D.Phil., New Medical School, University of Sydney ; p.r. 97 Beresford-road, Bellevue Hill.
1940		Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co., 1 O'Connell-street, Sydney.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Demonstrator in Botany, University of Sydney ; p.r. 17 The Promenade, Cheltenham.
1933	P 4	Voisey, Alan Heywood, M.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 8	Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney. (President, 1930.)
1940	P 3	Wade, Robert Thompson, M.A., Ph.D., 2 St. John's Court, Hunter-street, Parramatta.
1919	P 1	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney ; p.r. 45 Nelson-road, Killara. (Member from 1910-1913.)
1913	P 5	Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, F.A.C.I., Lecturer and Demonstrator in Physiology in the University of Sydney. (President, 1939.)
1921		‡Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., 39 Stanhope-road, Killara.
1924		Waterhouse, Leslie Vickery, B.E. *Syd.*, Mining Engineer, Shell House, Carrington-street, Box 58 CC, G.P.O., Sydney ; p.r. 4 Bertha-road, Neutral Bay.
1919		Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 5	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Reader in Agriculture, University of Sydney ; p.r. " Hazelmere," Chelmsford-avenue, Lindfield. (Vice-President.) (President, 1937.)
1941	P 1	Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of Agriculture, University of Sydney.
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney ; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1936		Wearne, Harold Wallis, 6 Collingwood-street, Drummoyne.
1920	P 39	Welch, Marcus Baldwin, B.Sc., A.I.C., Senior Research Officer, Forestry Commission of N.S.W., 96 Harrington-street, Sydney.
1920	P 1	Wellish, Edward Montague, M.A., Associate-Professor of Applied Mathematics in the University of Sydney ; p.r. 15 Belgium-avenue, Roseville.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1940	P 1	White, Douglas Elwood, M.Sc., D.Phil., Chemistry Department, The University, Melbourne.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, 143 Macquarie-street, Sydney ; p.r. Jersey-road, Strathfield.

Elected.		
1920		Williams, Harry, A.I.C., A.A.C.I., Frog's Hall Cottage, Aldham, Essex, England.
1940		Willison, Alan Maynard, M.Sc., 3 Stanley-street, Randwick.
1935	P 1	Wilson, Ralph Dudingston, M.Sc.Agr., Biological Branch, Department of Agriculture, Sydney.
1940		Wogan, Samuel James, 34 Neich-parade, Burwood.
1935		Wolstenholme, Edmund Kay, " Petarli," New South Head-road, Double Bay.
1936	P 1	Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Assistant Astronomer, Sydney Observatory ; p.r. 4 Ormond-street, Ashfield.
1906	P 12	Woolnough, Walter George, D.Sc., F.G.S., " Callabonna," Park-avenue, Gordon. (President, 1926.)
1916		Wright, George, Company Director, c/o Farmer & Company Limited, Sydney ; p.r. " Wanawong," Castle Hill, N.S.W.
1921		Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney ; p.r. Boomerang-street, Turramurra.

Honorary Members.

Limited to Twenty.

1939		Chapman, Frederick, A.L.S., F.R.S.N.Z., F.G.S., " Hellas," 50 Stawell-street, Kew, E.4, Victoria.
1914		Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1931		Lyle, Sir Thomas Ranken, K.B., C.B.E., M.A., D.Sc., F.R.S., " Lisbuoy," Irving-road, Toorak, Melbourne, Victoria.
1915		Maitland, Andrew Gibb, F.G.S., " Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912		Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.
1915		Thomson, Sir Joseph J., O.M., M.A., D.Sc., F.R.S., Nobel Laureate, Master of Trinity College, Cambridge, England.
1922		Wilson, James T., M.B., Ch.M. *Edin.*, F.R.S., Professor of Anatomy in the University of Cambridge ; p.r. 31 Grange-road, Cambridge, England.

Obituary 1941-1942.

Elected.	
1894	Richard Thomas Baker.
1935	Leon Macintosh Ellis.
1891	Edward George Noble.
1918	Carl Gustaf Sundstrom.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke " as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. " The Volcanoes of Victoria," and " The Origin of Dolomite " (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.

1907. " Geography of Australia in the Permo-Carboniferous Period " (two lectures). By Professor T. W. E. David, B.A., F.R.S.
" The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
" Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
" The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.

1918. " Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.

1919. " Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.

1936. " The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (This Journ., 1936, *70*, 39.)

1937. " Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (This Journ., 1937, *71*, 68.)

1938. " The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (This Journ., 1938, *71*, 503.)

1939. " Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (This Journ., 1939, *73*, 41.)

1940. " The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (This Journ., 1940, *74*, 283.)

1941. " The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (This Journ., 1941, *75*, 47.)

AWARDS OF THE CLARKE MEDAL.

Established in memory of
The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 *to* 1878.

The prefix * indicates the decease of the recipient.

Awarded.

1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
1879 *George Bentham, C.M.G., F.R.S.
1880 *Professor Thos. Huxley, F.R.S.
1881 *Professor F. M'Coy, F.R.S., F.G.S.
1882 *Professor James Dwight Dana, LL.D.
1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
1886 *Professor L. G. De Koninck, M.D.
1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.

Awarded.

1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
1893 *Professor Ralph Tate, F.L.S., F.G.S.
1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, C.M.G., F.L.S.
1903 *Alfred William Howitt, D.Sc., F.G.S.
1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
1909 *Dr. Walter E. Roth, B.A.
1912 *W. H. Twelvetrees, F.G.S.
1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, F.G.S.
1921 *Joseph James Fletcher, M.A., B.Sc.
1922 *Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925 *Charles Hedley, F.L.S.
1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
1932 Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.
1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
1938 Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
1939 C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

Awarded.

1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."

Awarded.

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. Burfitt, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (This Journal, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
1940 G. J. Burrows, B.Sc., University of Sydney.

ISSUED AUGUST 27, 1941

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OF NEW SOUTH WALES

FOR

1941

(INCORPORATED 1881)

PART I (pp. 1 to 46)

OF

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Containing Papers read in April and May, with Plate I

EDITED BY

THE HONORARY SECRETARIES

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN.

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CONTENTS

VOLUME LXXV

Part I

Page.

ART. I.—Presidential Address. By A. P. Elkin, M.A., Ph.D. (Issued July 4, 1941) 1

ART. II.—The Effect of the Synthetic Œstrogens, Stilbœstrol and Hexœstrol on the Pouch and Scrotum of *Trichosurus vulpecula*. By A. Bolliger, Ph.D., and A. J. Canny, M.B., B.S. (Issued July 4, 1941) 21

ART. III.—Magnetic Studies of Coordination Compounds. Part V. Binuclear Copper Derivatives of Diphenyl Methyl Arsine. By D. P. Mellor, M.Sc., and D. P. Craig, B.Sc. (Issued July 4, 1941) 27

ART. IV.—Progressive Rates of Tax in Australia. By H. S. Carslaw, Sc.D., LL.D. (Issued August 18, 1941) 31

NOTE.—In the interests of economy pages v-xxviii (List of Members) have been omitted from Part iv, Vol. LXXIV.

PRESIDENTIAL ADDRESS

By Professor A. P. Elkin, M.A., Ph.D.

(*Delivered to the Royal Society of New South Wales, April 3, 1941*)

Contents.

Part I. The Royal Society. Page.

The Past Year 1
The Function of the Royal Society 3

Part II. Science, Society and Everyman: Scientists, the Propagandists of Science.

The Royal Society and Anthropology 4
The Subject of this Address 5
Science and Everyman 6
Government Administration and Science 7
Scientists and Secrets 8
Scientists and Social Duty 9
Race Propaganda and the World Situation 11
"Half-Castes", Biology and Prejudice 14
Anthropology and the Administration of Native Races 15
Scientific Study of our own Society 17
Science, Education and Everyman 19

Part I. THE ROYAL SOCIETY.

The Past Year.

A feature of the past year in the Society's history has been the large number of members elected, namely sixty-two—the result for the most part of the efforts of one or two members. In the name of the Society I heartily welcome them and trust that they will continue " to run the race that is set before them ", in the fellowship of our Society ever pushing further away the boundaries of knowledge.

During the year we lost eight members by resignation and six by death. Our present membership stands at 307.

One of the very pleasant duties of the President—a duty which is usually a surprise to the newly-elected occupant of the chair—is to be official visitor to the New South Wales Observatory and in that capacity to attend a meeting of the Board of Visitors. I was fated to be the last of a series of Presidents who enjoyed the privilege of attending this meeting, with the late Mr. J. Nangle, a Past-President of our Society and Government Astronomer, as host, secretary and inspirer. Mr. Nangle and the two scientific members of his staff were performing very important work for science and the nation, indeed, for the world—for obviously there can be no boundaries to astronomy: the heavens are for all, even though the earth be partitioned out.

As you know, Mr. Nangle, even before retiring from the position of Director of Technical Education, offered his services as Honorary Astronomer, and

MAR - 3 1945

fortunately his offer was accepted. As it may not be possible for any person with the requisite qualifications to accept the position now under the same conditions, I am sure that I am speaking for you all in asking the Government to make such financial provision as will ensure the appointment of a Government Astronomer of distinction and the maintenance of an adequate staff for the continuation of the valuable work which is now in progress at the Observatory.

On my own and your behalf I sincerely thank the members of the Council and of the various committees and the office staff for their ready help and good work during the year; in particular, I thank the executive officers for the zeal with which they have performed their never-ending, though honorary, tasks—Mr. A. R. Penfold, Official Secretary; Mr. Welch, Honorary Treasurer; and Dr. C. Anderson, Editorial Secretary; also Mr. D. P. Mellor, who assisted the Editor, and Professor Earl, our Honorary Librarian. Nor do I forget the good work done by the Chairmen and Honorary Secretaries of Sections. Finally, I express my appreciation of the goodwill shown me by the members of the Society during my term of office.

The following statistics reveal some of the activities of the Society and its office-bearers. During the year there were nine general meetings, with an average attendance of fifty-three, at which forty papers were read; eleven Council meetings, with an average attendance of fourteen out of eighteen members. The executive officers kindly met me in consultation ten times, and there were eight meetings of special committees to deal with such matters as finance, rules, the appointment of Clarke Memorial Lecturer and Medallist and the Liversidge Lecturer.

Four Popular Science Lectures were arranged, and were well attended. The Society appreciates very much the help thus given by the lecturers: Phyllis M. Kaberry, M.A., Ph.D. (July 18, "An Inland People of New Guinea"), A. R. Woodhill, B.Sc.Agr. (August 15, "Insects and Disease in War-time, with Special Reference to Mosquito Biology"), R. N. Robertson, B.Sc., Ph.D. (September 19, "Energy for Living"), A. R. Penfold, F.A.C.I., F.C.S. (October 17, "Romances of Chemistry—Coal Stockings and Glass Ties").

The ninth Clarke Memorial Lecture was delivered on June 14 by Mr. E. J. Kenny, and was entitled "The Geologist and Sub-surface Water", and the Liversidge Research Lecture on October 31 by Mr. G. J. Burrows, B.Sc., on the subject "Organic Arsenicals in Peace and War". This was the third Liversidge Research Lecture delivered under the auspices of our Society.

As in previous years, your Council has endeavoured to make the general meetings of interest to all members. The highly specialised papers have been presented usually in very brief form, leaving time at three meetings for informative lecturettes ("Highlights of a Recent World Tour", by Mr. A. R. Penfold; "Submarine Canyons", by Dr. G. D. Osborne; "The Early History of Wireless", by Mr. G. G. Blake), and at another meeting for an explanation of exhibits (Ethnological by Professor A. P. Elkin and Glass Textiles by Mr. A. R. Penfold). In addition, almost the whole of the general meeting in August was devoted to a symposium on Potassium which had been organised by Mr. D. P. Mellor. The Lecture Hall was full. Prepared papers were read by G. de Vahl Davis, B.Sc.Agr., "The Commercial Potash Situation in Australia"; D. P. Mellor, M.Sc., "Some Aspects of the Chemistry of Potassium, with Special Reference to Potential Sources in Australia"; N. H. Parbery, D.Sc., "Potassium in Soil"; and R. N. Robertson, B.Sc., Ph.D., "Potassium in Plants". Mr. de Vahl Davis also showed a film entitled "The Mining and Manufacture of Potash in Europe". A number of persons present contributed to the discussion. Because of the importance of the subject, especially during the present international situation, the papers, together with the contributions made in the

discussion, were later printed as a booklet and distributed to members and others interested.

To sum up, at five out of the nine general meetings about half of the time (in one case, almost all) was devoted to subjects of general interest. At a sixth, the annual general meeting, all papers were read by title only to make time for elections and the hearing of the Annual Report and the President's Address. Thus, at only three meetings was the whole of the time—apart from formal business—expended on the reading and discussion of specialist-researches. If less time still were to be devoted to the latter purpose, it would mean that in most cases the papers would have to be read by title only. This would be a possible plan if they were read in full and discussed at previous section meetings, through which experience they might emerge with useful amendments. But it may be that the process would not stop there, for most sciences tend to be departmentally specialised, so that we might have subsections of sections. As against this, no doubt members like to hear at general meetings the results obtained by fellow members in their latest researches. The upshot is that we must seek a balance in the agenda of our general meetings, and, of course, as scientists, be not afraid to experiment with that agenda.

Function of the Royal Society.

Our Society has a threefold function : (1) In the first place, the Society exists to encourage research in all departments of science, art, literature and philosophy. It does this by providing a means of publishing worthy papers and an opportunity for discussing such papers and also subjects of scientific importance, and by awarding honours in the form of medals, money prizes and lectureships. These awards have been made possible by gifts from the late Professor Liversidge and Dr. Walter Burfitt and by the fund raised sixty years ago as a memorial to the late Reverend W. B. Clarke. For a period, too, 1882–1896, the Society, from its own current funds, awarded on fourteen occasions a substantial money prize, combined on twelve occasions with a bronze medal, as a reward and encouragement for research in various scientific fields. The award was actually made in each case for a particular paper. I suggest that when the financial position justifies the Society in so doing some such award as this should be renewed without limitation of the field of research.

In addition, the Society would welcome benefactions to enable it to increase its power of encouraging, and indeed of assisting research, not only by the awards of prizes, but also by making grants and awarding fellowships. Apart from such benefactions, the Society can do little more than at present, namely maintain the Journal and library and meet necessary and, incidentally, very moderate administrative expenses. To enable it to do this, your Council depends on the Government grant, for which we are all very thankful, on members' subscriptions, and on the income derived from the Society's limited amount of capital investment.

With regard to the discussion of research results, as I have already suggested, the formation of more sections might be encouraged ; for example, in Chemistry and Sociology. In this connection the Council regretfully accepted during the past year the dissolution of the Physics Section which, after fifteen and a half years of useful work, prepared the way for the formation in Sydney of a branch of the Institute of Physics.

(2) The second function of our Society is to give all members an opportunity for becoming acquainted as soon as possible with the results of recent research ; in other words, to enable specialists in the various branches and also what may be called " lay members " to keep abreast of scientific advances in general. This is the object of the general meetings, with their brief explanations and

discussions of papers and lecturettes. The informal talks during supper can also help in this direction.

(3) The final function of the Society is its "popular" work—the passing on in acceptable form of scientific knowledge to the general public. At present, we rely mainly on four or five public lectures a year given in an honorary capacity by experts. I believe we would be rendering service to the community by expanding this part of our work, if we had the funds—a subject to which I will return in a later section of this address. If we could not do this directly, we should try to do so indirectly, that is by urging, inspiring, assisting and co-operating with other scientific and educational groups to spread scientific knowledge and the scientific attitude.

In concluding this part of my address, I express regret that owing to the present time of international strain which affects each one of us, the Annual Dinner was not held. Your Council at first planned to hold it, but as the weeks passed by I formed the opinion that our Society should refrain from any function, the purpose of which was solely pleasurable, and with this opinion both the executive officers and later the Council expressed agreement. Incidentally, the dinner was not held during the war of 1914–18. Our next dinner (and may it soon be held) will celebrate the cessation of hostilities and the dedication of the energies of scientists to their share of the work of rehabilitation of society on a peace basis.

Part II.

SCIENCE, SOCIETY AND "EVERYMAN"

OR

SCIENTISTS, THE PROPAGANDISTS OF SCIENCE.

The Royal Society and Anthropology.

The Presidents of the Royal Society have come hitherto from many departments of science—agriculture, astronomy, botany, chemistry, engineering, geology, mathematics, physics, physiology, statistics, veterinary science and zoology. It is interesting to notice that while all these subjects are of vital importance to man if he is to understand the universe in which he finds himself, none of them are directly concerned with the phenomenon of man himself as a thinking and social being. In 1940, however, you drew your President from the field of the social sciences, a term that is coming into vogue, in particular from anthropology—and more precisely from social anthropology, which is sociology writ wide and large.

This is not the first recognition given by our Society to anthropology. Many papers on the subject have been published in our Journal, especially between 1890 and 1910.[1] The Society's money prize was awarded in 1882 (John Frazer), 1889 (Reverend John Mathew) and 1894 (R. H. Mathews) for papers on the Australian Aborigines, and three of the recipients of the Clarke Memorial Medal, A. W. Howitt (1903), W. E. Roth (1909) and Baldwin Spencer (1923), whatever other accomplishments could be credited to them, will live in the annals of Australian science for their contributions to our knowledge of the Australian Aborigines.

The election of a social anthropologist, however, to the very honourable position of President of the Royal Society of New South Wales in these latter days is very significant. Wittingly or unwittingly, in so doing you have

[1] From 1870–1889, 12 papers; from 1890–1899, 23 papers; from 1900–1909, 18 papers; from 1910–1940, 9 papers.

expressed what I think is one of our greatest needs today—the scientific study of human society ; that is, the endeavour to ascertain the principles of social structure not only in itself but also in relation to culture and change, to understand the laws of social and cultural change and to clarify the relation of society to the individual, his thoughts, feelings and actions. I cannot take time here to develop this point further, but must content myself with saying that sociology can be and must be as scientific in its methods, techniques and objectives as any other science, pure and applied.

The Subject of the Address.

Until 1900 the annual address to the Society was termed the Anniversary address, and up to 1880 was delivered by a Vice-President of the Society. The Governor, who was President of the Society, was spared this task. From 1881 to 1900, the address was delivered by the President, who, however, was no longer the Governor, the latter having been made *ex officio* Honorary President of the Society by a rule adopted in 1879, and Vice-President on a revision of the rules in 1901. But be he President or Vice-President who delivered the annual address, he was generally somewhat perplexed regarding its subject matter. As one put it forty years ago : " There comes the important question as to what rightly constitutes the subject matter of the presidential address : whether it should be a retrospect of the scientific work of the year, an announcement of something new in science, a history of science brought to date, a discussion of some ' burning question ', or merely a dissertation on some particular subject passing in the mind of the President." Fortunately there is no rule governing the matter of the address, nor indeed is there a rule that one should be inflicted on the President and members. Tradition, however, steps in and prevents him from escaping its preparation and constrains a quorum to be present during its delivery. Tradition, too, is the main factor in determining the general outlines of the address. Almost all have contained brief references to events of interest and significance in the life of the Society during the preceding year, including the year's register of obituary notices of members, a necrology, as three Presidents aptly termed it. For many years too, the address included a survey of the year's advances in all departments of science the world over—an undertaking which grew more formidable each year until at last, in the first decade of this century, in face of the increased specialisation within each science, and of the great growth of scientific work in country after country, the President wisely shrank from the task ; instead, he confined himself either (*a*) to unburdening himself of some thoughts which came, " perhaps unbidden ", to his mind during the year, or (*b*) to giving a survey of research, discovery and application within his own specialised sphere of work, and/or (*c*) presenting the results of a definite piece of research carried out by himself. The addresses for the last thirty years have tended towards the establishing the third as a tradition, though it is sometimes combined with the second. Fortunately, however, this has not quite scotched the urge of an occasional President either to devote the whole of his address to " unburdening his mind ", or else to making his survey of specialised scientific advance the basis for some degree of " unburdening ". In other words, all scientists cannot all the time keep within the academic cloisters and the laboratory, but are constrained to speak directly to the general public or to the government on matters of practical significance arising out of their special studies. It is good that this is so, and may the tradition of this Society never be set against such breaking forth from the scientific cocoon ! " Science for the sake of science " is a noble motto to be observed during research, although " science for the sake of business " or " of war " is not unknown. But in any case, science was made for man and not man for science. It has come into being for the use of man ; it is a means by which he learns to understand

and adapt himself better to and even use his total environment—material, human and social. Life is *the* task, and science one of the means by which man performs that task.

Science and Everyman.

It is a chastening thought to realise that science, aye and scientists too, mean very little, usually nothing, to the average man. It is true that the latter has gained from the scientists' discoveries, which underlie the telephone, radio, motor car, aeroplane, electric sweeper, the " talkies " and so on, but to " Everyman " the great majority of these things mean no more than the magic lantern and steam engine did to people of other days. The present generation grows up quite accustomed to them. I am concerned, however, not so much with the material benefits bestowed by science as with man's attitude to the world, to life in the world, and the problems related thereto. One social scientist ventured to predict that with increasing scientific knowledge—psychological and sociological as well as natural—the cohesion of society would be ensured and man would live a moral life without any reference to religious sanctions and the sphere of the contingent with which these are interrelated. " Psychology ", he said, " will in the future enable us to construct a truly scientific scheme of education and child training. If in the distant future biology should show us how to breed a better race, science will ultimately give man a new self . . . .The social sciences may be expected to yield up the secrets of social order and progress and thus enable man to perfect his social system. Meanwhile, there need be no fear that, if men cease to believe in God, they will straightway prepare to go to the devil . . . .The moral code based on the mandates of God yields slowly but surely to one based on the mandates of science, but the new morality is doubly strong. It not only makes its own appeal to the human reason and the desire to live long and well, but it has back of it the same social sanction which compels conformity everywhere."[2] This author has obviously very great faith in the logical character of man's conduct—at least in the far distant future ; his is a vision of a future which he desires. But I doubt whether the facts allow us so to dream, and those facts are human beings as they are and as they have been. Most of our behaviour is based not on scientific knowledge and logical deductions therefrom, but is non-logical, arising from our desires and from the attitudes which we have imbibed from, or which have been inculcated in us by, our society or by some group within that society. It is all too easy to say that we are living in a scientific age ; we are living in an age in which there are very many scientists and in which much practical use is being made of scientific research, but the comparatively many scientists are but a very small minority of the population, and again, a very small minority of the latter has any worthwhile appreciation of science or of the scientific attitude to life and its problems.

In spite of school curricula, of scientific subjects in the Leaving Certificate and of popular science on the radio, you will be fortunate to find in a township, or indeed in many suburbs, apart from scientific teachers and workers, more than half a dozen individuals who know anything about scientific method, scientific attitude or " scientific mandates ". The proceedings of scientific bodies is not considered news by the papers. Moreover, a very strong proof that our age is not scientific is provided by the flourishing existence of Christian science and astrology, the former with its refusal to face unpleasant phenomena, and the latter with its removal of human responsibility for decision to the accident of birth in relation to the stars—a witness to the gullibility of human beings. Then there is British Israelitism, with its convenient proofs from the

[2] F. H. Hankins, *An Introduction to the Study of Society*, pp. 596–7.

Great Pyramid and the Bible, or Jehovah's Witnesses with their effective salesmanship of their propagandist literature. Probably few if any of the members of our Society are interested in these and similar cults, but hundreds of thousands of citizens are keenly interested in them and many more nibble at the baits which are extended. These cults are mostly paying concerns and in some cases are organised on an immense scale. But if the social disciplines of psychology, anthropology and history, and the natural sciences of astronomy and biology really contributed to the stock-in-trade of the average man, this would not, or at least should not, be so. In other words, the scientific knowledge and attitude possessed by a few is unknown to, or ignored by, very many who are therefore the mental, social and financial prey of strange cults and superstitions. In the face of the contingencies of life, of the unknown and of disasters, they return to the primitive or the mediæval—to astrologer, anthroposophist, " medicine-man healer ", or the soothsayer whether he use the stars, the pyramid, the Bible or the séance.

What is the explanation of this phenomenon? Some say it is a sign of the general neurosis which has overtaken our age, itself the result of the vast speeding up of the pace of life—the consequence of mechanical advance. Others say it is the fault of the churches for not giving people a saner attitude when faced with life's difficulties and disasters, or they blame the education system, which is said to be concerned overmuch with preparing children to make a livelihood, instead of equipping them to recognise and meet squarely and sanely the problems of life as they arise and to solve them consciously and logically. But scientists and scientific bodies must acknowledge that they themselves have not done all that they should have done. The age is not scientific because the scientists have persuaded neither the authorities—political, administrative and educational—nor the people generally that they *should* and *can be* scientific, that science provides not only a content of knowledge and a means of increased efficiency and pleasure, but also an attitude to life.

Government Administration and Science.

Another sign of this failure is the lack of appreciation by governments of the co-operation which they could receive from scientists—an unfortunate fact about which much has been heard since the threat and outbreak of this war. Scientists and scientific bodies when offering their services have been nonplussed when told that there was nothing for them to do. The members of one scientific group were told to get in touch with their respective air-raid wardens—advice which takes us to the root of the trouble. It is not merely that Cabinet ministers think that everything possible is no doubt being done by the experts in the various government departments, or (as is sometimes said) that these latter do not welcome outside assistance, but that ministers and departmental heads are usually typical examples of "Everyman", that is, they have no more grip of the significance of science for human thought and well-being than the latter. Therefore, in face of the scientists' offer of service, they are genuinely nonplussed, for do they not hold the usual opinion that the scientist—professor or not—spends all his time in his laboratory, like a chrysalis in its cocoon, and has no understanding of practical affairs? Moreover, government and administrative heads, knowing their own power, believe that all contingencies and problems can be met by administrative efficiency—by additional administrative officers, if necessary. And so persons renowned for their business acumen and administrative abilities are appointed to this or that service, often irrespective of the content or specialty of the particular department. A good administrator is held to be a person who not only can grip all the details of a particular department and task in a few months, but also can understand the problems associated with it, be these human or scientific. Of course, good administrators are required

for public affairs in both peace and war, but apart from the fact that some scientists are good administrators, the really good administrator for many departments of life these days should be one whose training has taught him to understand the scientific attitude, to appreciate the relation of scientific experiment and discovery to national welfare, and, when confronted with important problems, to be prepared to call upon the scientific resources and potentialities of scientists engaged in the particular sphere which is in question. This, of course, would be done most simply through the organised scientific bodies such as our own, the Australian National Research Council, and any nation-wide register of scientists which is in existence. Such help would then be used in collaboration with the Council for Scientific and Industrial Research and the departmental scientific experts.

A very sad feature of that most interesting recent Penguin Special, *Science in War* (1940), is the revelation of the small degree in which science and scientists were being used in England quite recently in the war effort, and of the inefficiency and serious consequences which followed from this state of affairs. It is stated that the group of scientists who still stand outside war work and who include some of the most powerful minds in science, " has no knowledge, except in the most general terms, of the problems by which the country is faced ". Unfortunately too, those scientists who sit on government advisory boards and committees or conduct extra-mural war work in their laboratories, seem unable to do more than agree with government decisions, instead of challenging them when necessary in the name of science. Various examples are given in this book of the way in which science could help the war effort if it could be effectively heard and used. Thus : " there is little doubt that geographic and economic knowledge and the assistance of great modern developments in mathematics could lead, in a minimum of time, to a revolution in strategy far greater than that introduced by Napoleon ". Again, in air warfare, while many problems have been dealt with effectively by science, " others could be if government departments were willing to carry out proposals based on scientific study " ; and with regard to bomb shelters, the scientific approach, which is briefly summarised, was made outside official circles before the war and " its application was strenuously resisted by the government department concerned ". Other examples are provided by the camouflage methods—an extraordinarily convincing instance of the ineptitude of the existing system where science is concerned, by the provision of food in war time and so on.[3]

The picture is becoming less gloomy, thanks to the course of the war and much agitation on the part of scientific bodies. In Australia, the Commonwealth Government is becoming gradually seized with the necessity for making a survey of available manpower and resources, which could be used wherever and whenever required in the present national emergency—but so far it has been a piecemeal process instead of being part of a planned unitary scheme. In addition, advisory panels have been set up, including, or consisting of scientists, and a number of individual non-Government scientists are working on war problems under the auspices of various government departments.

Scientists and Secrets.

Incidentally, a matter of some psychological importance arises in connection with this. Scientists whose services are used to assist the war effort on panels or in research, not only become acquainted with and contribute technical processes of a secret nature ; in addition they are supplied with confidential information regarding the seriousness of the war itself or the country's situation with reference to this or that vital necessity, so that they may be fully seized

[3] *Science in War*, pp. 12–13, 35, 43, 91.

with the significance and importance of their work. Needless to say, they will not discuss such information with any person outside their particular panel or board; but they are not so accustomed to possessing secret information of vital significance as are for example members of the diplomatic service and father confessors. This is as it should be, because normally there is nothing confidential about the objects, methods or results of scientific research, all of which are displayed for the benefit and interest of all who desire to use them. But in the war situation a good deal of emotional tension is apt to be created—a tension which occasionally breaks, and reference is made, possibly in the course of discussion, to one's possession of confidential information, though details are not mentioned, with the effect that one's arguments may seem irresistible.

This is quite understandable, for scientists, in spite of cartoons, are normal human beings, "of like passions" with other men. In certain critical circumstances all of us are apt to be less than scientific and to appeal to the emotions rather than to an array of facts carefully observed or experimentally tested. But in the realm of what might be termed vital information, unless the cards can be put on the table, let them be kept in the table drawer, with the drawer shut. No references should be made to what cannot be disclosed. This applies of course not only to scientists, but to governments and national leaders, all of whom should give to one another and to people at large definite information only, be it good or bad; this can be faced and dealt with. But they should not make suggestions of possible national "time-bombs" about which they know something but can reveal nothing except a feeling of anxiety. It is the duty of administrations, together with the help of scientists when necessary, to render those "time-bombs" harmless, be they economic, military or international, or else to prepare as fully as possible for the explosions. The cohesion and unity of society which is so important in time of war depends, like the success of a scientific experiment, on a positively formulated plan based on all available knowledge. Such knowledge must be shared out on a basis of cooperation in the tasks to be accomplished. But cohesion is weakened by creating emotional tensions on the basis of suggested but concealed knowledge regarding national difficulties, handicaps and possible disasters. And since the psychological and sociological principles involved are well established, scientists will not only observe them in their own work and attitudes in time of national crisis, but will ask the governments also to bear them in mind.

Scientists and Social Duty.

This brings me again to my theme that if scientific societies and scientists possess knowledge and understanding which would make for the welfare, cohesion and progress of society, or prevent disintegration of society or the confusion of its individual members, then those scientists are as citizens bound to do their utmost to press their knowledge on both government and people. We should not sit aloof adopting the attitude that if the country does not want our knowledge or help it can leave it. In doing this we become morally responsible for the continuation of unsatisfactory conditions, or for disasters which could have been avoided had our knowledge been used. It may be that some scientists are temperamentally unsuited for the necessary propaganda work which is involved, and that persons who are not themselves research workers but who do appreciate the practical and national significance of science, are better fitted for it. Against this, however, is the fact that the scientific specialist can speak with authority, and if he possess the necessary patience and persistence, eventually he will be heard. In any case, scientific societies, such as our own, could undertake this essential national work in which they would be guided by their own expert committees or sections. Suppose for example that

immunisation against some epidemic diseases such as diphtheria were regarded as of sufficient importance and effectiveness to justify a campaign to ensure its voluntary universal practice, then such a society as our own might well set up an expert committee of medical scientists and chemists to examine the evidence, and if this committee reported against the practice, the fact should be communicated to the authorities as well as to the public. If, however, the report justified the practice, the Society, in addition to informing the health authorities of its finding, might well support their campaign by arranging for a public symposium, popular lectures, wireless talks, newspaper articles and pamphlets, in all of which the scientific basis and proof as well as the statistical results of the practice would be set forth. Such action on the part of a disinterested and purely scientific body would be of great support to the health authorities' campaign, and could not be dismissed as a mere fad of the health department. Of course, such scientific body would carefully avoid all political entanglements.

I have mentioned immunisation as an example because so many people are still worried about it and, with regard to diphtheria, there has been a campaign against it. The subject is of national importance, and therefore a scientific body would be doing a national service by endeavouring to get a scientific attitude adopted by the public towards it, and by spreading a knowledge of the facts. As another example, I could refer to the danger of overcrowding of civilians or soldiers in camps without satisfactory precautions against uncleanliness, with the consequent risk of typhus or other epidemic diseases, as was pointed out in one of our popular lectures during the past year.[4] In this case, if events warranted such action, our Society, probably through a select committee, should back up the efforts of the specialist by putting the scientific facts before the Government and the particular administrative department (military, works or other). At the same time it should make the public conversant with them so that public opinion would be ready for, and indeed would ask for, the necessary administrative action. Examples could be taken from other spheres : biology, agriculture, astronomy, physics, and so on.

The suggestion of this line of social propagandist action for such a society as our own is evolutionary, not revolutionary. The object of our Society, as expressed in its Act of Incorporation, is to encourage studies and investigations in science, art, literature and philosophy, to which is added in Rule 1 the significant words, " especially on such subjects as tend to develop the resources of Australia ". Moreover, in the course of its history it has adopted the plan of holding popular lectures as a means of disseminating to the man in the street, in understandable form, the results and importance of specialist-research. The suggestion is that we and all scientific bodies do more of this, and also when circumstances demand, press our knowledge and attitude on governments and people alike—if necessary with the persistence of the importunate widow. Certainly we should not adopt the " take it or leave it " attitude. We are citizens, and our best contribution must be through our specialised disciplines, not merely to be stored in learned journals steadily mounting until our articles have reached the century mark, but also, if the material be appropriate, to be added to the life and thought of " Everyman ". Scientific groups belong to the body politic and are not only concerned with the academic pursuit of science and occasionally with related issues such as the exportation of fossils and the preservation of fauna and flora ; they must also watch over and contribute to the well-being of society as a whole whenever their special knowledge enables them to do so. If the public is being misled by dangerous propaganda and is mistaken on significant

[4] A. R. Woodhill, " Insects and Disease in War-time, with Special Reference to Mosquito Biology ", Royal Society of N.S.W. Popular Lecture, August 15, 1940.

matters and we know the facts, then we must make those facts known. At times, scientists must be propagandists.

Needless to say the term propaganda as I use it here contains no suggestion of misrepresentation, but means, as in the dictionary definition, the dissemination of principles and knowledge so that these may bear fruit in the life of man and society. Misrepresentation may be used in propaganda, but not by scientists. On the other hand propaganda of the false can be counteracted most effectively by propaganda of the true.

Race Propaganda—and the World Situation.

Let me now illustrate my theme with a subject from the anthropological sphere, namely " propaganda and the concept of race ". The idea had grown up—especially a century or more ago—of " the complete separateness of certain populations ", and this was exploited by propagandists who discussed racial questions for national or political ends. But physical anthropologists have known for decades that there is no sharp grouping between the races of mankind, that is if the term race be used in its only valid sense, as a biological concept, without any reference to culture in general, or language in particular. It is interesting to notice that the first investigator to maintain that human races formed a continuous system with distinguishable parts but no abrupt divisions was a German, J. F. Blumenbach,[5] whose work has obviously been ignored in propounding official racial theories in modern Germany. All recent research confirms Blumenbach's contention. Apart from the ideal conceptions we have of the four main divisions of mankind (or major sub-species) into European or Caucasian, Mongol, Negroid and Australoid, the division into biological races, that is the inheritance of group characteristics, is a statistical matter, for so-called races both shade off into and overlap one another. We have fairly clear pictures of such ideal types (or minor sub-species) as Nordic, Alpine and Mediterranean, but we find few pure examples of these types, the result of diversity in prehistoric and early historic times, of migration, of intermarriage, and of the influence of environment on certain physical features. Thus, if we pass from Scandinavia and Finland south to the Sahara, where shall we draw the various racial divisions, or if we travel from Ireland east to Siberia and Japan, will our task be any easier? The fact is that there is no population in Europe today which can be sharply divided off from neighbouring peoples on the basis of racial distinctions. On our journeys we pass through various nations, or countries as we frequently call them, but as the result of the study of such significant biological features as head-form, body height, hair form and colour, skin and eye colour and blood grouping, we realise that such unity as each nation possesses is not the consequence of its supposed unitary racial origin, but is a *cultural factor*, built up during the course of history. Even Germany, while possessing a number of blondes in its population, is the outstanding example of a *national* European group consisting of a number of sections which differ markedly in their physical characters. Likewise, while there is, or was, a French nation, there is no French race. Conversely, some peoples think they are racially quite distinct from their neighbours, when there is no such distinction, but only a marked difference in language and, possibly, in other cultural

[5] His works on the subject were published in Germany in 1775 and 1795, and translated for and published by the Anthropological Society of London in 1865 under the title of " The Anthropological Treatises of Johann Friedrich Blumenbach ". *Vide* T. K. Penniman, *A Hundred Years of Anthropology*, pp. 55–6, 373, and G. M. Morant, " Racial Theories and International Relations ", *Journal of the Royal Anthropological Institute*, London, Vol. LXIX, p. 153. *Vide* also F. H. Hankins, *An Introduction to the Study of Society*, pp. 93–6, for further reference to Blumenbach and a discussion of overlapping of races. Also C. S. Coon, *The Races of Europe*, 1939, pp. 251–96, for a similar but more recent discussion.

elements. For example in 1939 the Finnish Government announced that the Finns had neither national nor racial affinity with Russia, and that the Finns are Nordic in character. But " the evidence of physical characters shows unequivocally that Finns and white Russians are closely allied, and it fails entirely to indicate any line of division between them which might be correlated with a national or linguistic frontier ".[6] Again, the Czechs of Bohemia regard themselves as Slavonic and used to dream of a union of all the Slavonic peoples of Europe, but racially they are closely allied to the neighbouring peoples of Germanic speech and " this racial bond is much more intimate than that between the populations of western and eastern Germany on the one hand or those between the Czechs and many Slavonic peoples on the other ". The Slavonic characteristics of the Czechs are cultural rather than racial (biological), the result of an historical accident—their conversion to Christianity from the East. Had this influence come to them from the West, they would have become Teutonic in culture and speech.[7]

The point is that race is not related to nationhood or culture either logically or biologically, but only through the happenings of history. We must bear in mind and indeed promulgate the following facts :

(1) A nation may consist of more than one race.

(2) The same race may constitute part of more than one nation.

(3) In every or almost every case some groups of people in neighbouring nations are closely related racially, and that as far as Europe is concerned, any war between national groups is in some degree or other racially a " civil " war.

(4) While a racial group possesses distinctive hereditary traits in spite of variations around the particular racial type, racial types are relative and in a state of flux and, in characteristic features, shade off into one another ; therefore to speak of a nation as a pure race, or indeed of a race as being pure, is in almost every case biological and racial nonsense. This applies, of course, to the Nazi doctrine that the Germans are pure Nordics.

(5) The so-called " race consciousness " of which we hear at times and which implies that a people possess a feeling of unity and of distinction from other peoples because its members share a common descent, is a pure fiction. There may be a strong national consciousness, based on contiguity, historical continuity and community of economic and political life, but this national group may ultimately be made up of individuals or even small groups sprung from several racial sources. Consciousness of community is an *historical accomplishment, not a racial inheritance* ; and it is this, not race, which is the basis of true nationhood.

(6) Another baseless fiction is the doctrine of Nordic supremacy, that is to say that a certain racial group, distinguished by fair hair, blue eyes and tall stature, was by reason of something in its biological inheritance the creator and organiser of all civilisations, and is the only hope of the future. The foundation of the doctrine appeared in the work of Count Arthur de Gobineau, who in 1853 declared that the fundamental factor in the development and decay of civilisation

[6] G. M. Morant, " Racial Theories and International Relations ", *Journal of the Royal Anthropological Institute*, Vol. LXIX, p. 161. Also C. S. Coon, *The Races of Europe*, 1939, pp. 359–67, 568 and maps, pp. 176–7, 294–5.

[7] G. M. Morant, *op. cit.*, p. 161. *The War and Democracy*, by various authors, 1914, p. 70. C. S. Coon, *op. cit.*, pp. 560–2 and map, pp. 294–5. Professor Coon writes that zoologically the Czechs are descendants of early Slavic immigrants who, like all Slavs, were primarily Nordic. But the Czechs changed in form during the centuries until from the point of view of measurements they became Alpine in head and face, while their colour is as fair as in the case of most Southern Germans.

is racial, and that if the fundamental racial constitution be engulfed among other races to such an extent that it ceases to exert the necessary influence, both the people and civilisation will die out. In 1895 H. S. Chamberlain maintained that " the Teutonic stock was the real creator of present-day civilisation and our best hope for the future ".[8] The use made of this false theory by Nazi Germany is well known, and just as well known to students is the fact that the doctrine is *politically inspired and not anthropologically based.* Germany is not a pure race—even with all the Jews ejected—and as we have seen, racial groups shade off into one another ; moreover, civilisation is built up by the experience and contributions of many races and nations. There are valuable cultural crossings and diffusions, as well as racial crossings and immigrations. But, of course, the Nordic theory or any similar theory of racial superiority, appealing as it does to a people's vanity, can be used with great effect in unifying a people and arousing enthusiasm for some cause, be it the spread of German *kultur* as in the last war, or the spread of Nazism today. As one writer puts it, " in adopting beliefs regarding racial theories, most people are prepared to become followers of a cult ; few will show any inclination to become students of a science ".[9]

I am drawing your attention to these anthropological facts and principles not merely because of their importance and interest, but because they have not entered into the working mental equipment of the public (voters) or governments in our own country or the world at large, and because scientists, to wit anthropologists, must bear the blame for this. The ideas which people hold regarding race, nation and culture are usually so nebulous that they can be easily swayed by astute propaganda ; moreover, racial preaching is apt to grip peoples' imagination and stir their enthusiasm in a remarkable and indeed overpowering manner, for it appeals both to man's interest in his past and to pride in his future. A somewhat inoffensive example is provided by British Israelism. But the same cannot be said of the Aryan racial propaganda of Germany, nor indeed of the ridiculous plea made by Professor Carmelo Midulla for the recognition of an " Aryan and Mediterranean " type as the Italian national " archetype ", which incidentally is said to approximate in measurements to the statues of Apollo Belvedere and of Venus (of Cyrene and Venus Anadyomene). This plea could be none other than an attempt to bolster up national pride, political in intent, for scientifically it is absurd both as regards the method of selecting individuals and of striking averages in the measurements, and also in the use of the term Aryan-Mediterranean, which is apparently a blanket term used to cover either two distinct divisions of mankind or else a linguistic and a racial grouping. No doubt it is meant to convey the idea that the Italian Mediterranean people are to be distinguished from other peoples of Mediterranean stock, such as the Jews, Arabs and Abyssinians, and to be affiliated with that supposed Aryan race which not only originated the basic Aryan tongue but also alone possesses the powers to develop a truly advanced culture. At least this would show that the Italians are fit partners for Hitler.[10]

Of course, anthropologists knew quite well that these theories were ill-founded and were propounded for political and national aims. F. H. Hankins, for example, examined and exposed them in his *Racial Basis of Civilization*

[8] T. K. Penniman, *A Hundred Years of Anthropology*, pp. 84 and 126. For a full examination of the theory, *vide* F. H. Hankins, *The Racial Basis of Civilization.*

[9] G. M. Morant, *op. cit.*, p. 158.

[10] Strictly speaking too, Aryan is a linguistic term and has no reference to race ; but Hitler and apparently this Italian professor also use for their own purposes the old mistaken idea that race can be determined by language—by linguistic origin ; thus an Aryan people is one which speaks and is sprung from Aryan-speaking ancestors. Italy consists mainly of Mediterranean peoples, but the Alpine racial type and to a less extent the Nordic type is found in northern Italy. With regard to Midulla, *vide* " Aryan and Mediterranean Anthropometry ", by C. Suffern, *Man*, December, 1939, pp. 199–200.

(1926), and more recently A. C. Haddon and Julian Huxley provided a most helpful survey of the racial make-up of Europeans in their book *We Europeans* (1935). And students in the few anthropological classes in the British Empire and in the somewhat greater number in America also became acquainted with the facts, but the knowledge was not broadcast and impressed on the general public—on " Everyman ". And what is worse, when the propaganda regarding racial distinctions which was broadcast before the war, especially in Europe, was doing much to embitter international relations, anthropologists did not make any effective protest. They knew the facts, they recognised or could have recognised the hollowness of some continental theories and their political motive, and they should have tried by means of public lectures, pamphlets, newspaper articles and wireless talks to expose the fallacies and broadcast the truth in their own and other tongues, and should have done so tirelessly. It is true that if this campaign had been successful, the Nazi propagandists might have found some alternate theme to serve their purpose, but to make the other side shift its ground through the exposure of inherent fallacies is to cause at least some degree of lack of confidence and loss of equilibrium. In any case, the duty of anthropologists was clear, but it was not performed. The principal reason for this failure was no doubt the doctrine that scientists should not interfere in political and practical affairs, although they might criticise them learnedly within the academic precincts and in esoteric publications.[11]

Let us hope that when this war is over and boundaries in Europe and North Africa and perhaps elsewhere have to be arranged anthropologists (and historians too) will be summoned, or will persist in being summoned, to the pertinent international committees, and will ensure that there be no confusion of race with culture or of either with nation, and that all divisions of populations on so-called racial grounds be very carefully examined before being made the basis of continuing or of establishing national boundaries.

" Half-Castes ", Biology and Prejudice.

An example of the confusion of biological inheritance with cultural factors comes from our own country—a confusion arising from ignorance. It refers to the people of mixed European and Aboriginal blood in Australia, often called " half-castes ", irrespective of the proportion of Aboriginal and European ancestry in each case. We frequently hear it said, even in high places, that these folk inherit the vices of both races. But the word vice has reference only to standards of behaviour and is solely of cultural significance. Some Aborigines are vicious according to Aboriginal moral standards, just as some Europeans are vicious according to European standards. There is no evidence, however, to show that half-castes should in some remarkable way inherit vices from their two parents which possibly the latter did not exhibit. Nor indeed is there any evidence to show that moral standards or vice and virtue are biologically inherited. On the one hand moral standards are evolved during a society's history, and on the other hand vice and virtue are accomplishments developed during an individual's history as the result of training and reaction to his environment—home, society, economic conditions etc. They are cultural phenomena. With regard to half-castes it is sufficient to say that if any of them exhibit the vices of both races it is because they belong culturally to neither. They have not learnt the standards and sanctions of Aboriginal society and, being treated as outcasts by us, they have neither received the same early training as we, nor any real assurance of an effective place in our

[11] The responsibility of anthropologists in this particular has been elaborated by Dr. G. M. Morant in *The Races of Central Eruope* (1939) as well as in his article " Racial Theories and International Relations ", *Journal of the Royal Anthropological Institute*, Vol. LXIX, 1939, pp. 151–62.

social and economic order, with the result that in some cases they throw restraint to the winds or become resentful and suspicious. The point is that their so-called vices are culturally determined, and the responsibility is ours even more than theirs.

This criticism of half-castes is related to our colour prejudice, which again is a cultural attitude developed and possessed by British folk, but not by some other European peoples. It is not innate nor biologically founded, and incidentally is by no means strong enough to prevent miscegenation between British men and Aboriginal women. The antipathy is sometimes rationalised on the basis that the half-castes are not well washed, live in dirty conditions and are not educated, and so we prefer not to admit them to our schools, hospitals and churches. These assertions are true in a number of cases, but they can be overcome with patience, water, training and fellowship.

Anthropologists, knowing that the objections to half-castes are cultural and not biologically founded, must say so, especially to the general public, and thus clear the ground for an honest tackling of the " half-caste " problem in this continent.

Anthropology and the Administration of Native Races.

My next illustration of the theme that science must make itself effective in the life and thought of people is taken from a related sphere which should be of interest to all of us—the administration of native races—for we in Australia are directly concerned with our Aborigines and the natives of Papua, the Mandated Territories of New Guinea and Nauru, and in a less degree with all the native races of the British Empire. Good administration as distinct from repression and slavery is not based simply on a knowledge of what a native people can do for us or of what we can derive from its country, but (*a*) on an understanding of that people's social and religious organization, (*b*) on the conviction that it possesses a pattern of culture which has been built up in the course of its history and which serves it more or less well in adjusting itself to environment and to the changes which occur in the course of time, and (*c*) on a study of the facts and problems of cultural and " racial " contact and of change. Now these three prerequisites of good administration are the special concern of social anthropology. A few administrators and missionaries had realised these facts, even though " through a glass darkly ", but it is only the specialised work of trained social anthropologists during the past three or four decades which has enabled us to understand the life of primitive societies ; and, incidentally, to evaluate the commonly held clichés, not all inoperative today, such as the savage is magic-ridden, weighed down by superstitions and overwrought by fear ; he has no law, and yet is helpless in the power of tradition and consequently is ultra-conservative ; he cannot adapt himself to our culture, but is a member of a child-race and must be treated as a child ; and so on.

As a result of research, we no longer regard the so-called savage as a queer individual with a number of strange beliefs and quaint and maybe horrible customs which it is interesting to record, before his old ways have been completely changed, or he and his fellows have ceased to exist upon the earth. This is the view of the collector—the museum-exhibit attitude. Instead, we now have a living and dynamic approach, sometimes called functional. We look at primitive society as a living whole, the present stage in an historical process. This society, just as in the case of a civilised society, consists of its individual members grouped in various ways on the bases of contiguity (locality), kinship, age, sex, economic pursuit, religious cult and one or more social interests. Thus there are families, kinship groups, occupational groups, sex and age groupings and cult groups. Clans, moieties, social ranks, castes and political groups are

found in some primitive and other societies.[12] The actual forms and numbers of these groups depend on historical happenings and conditions, such as the environment, the economic situation (food supply aad possibilities of developing arts and crafts), the size of population, contact with other peoples and cultures, and the rise of leaders. But the point is that the various groups of any one society function together, and society's task is to maintain a state of equilibrium—not necessarily static—a condition which will be reflected in the lives of its individual members, for each one is a member of several if not of all the different types of groups in his society, religious, occupational, sex, age, kinship, clan, family and locality. He has several loyalties, and on the working out of a system of loyalties depends not only his own mental and social well-being but also the well-being of society. Of course, tradition helps in this. Thus life, even in a primitive society (Papuan or other) is a social task which has relation to the history and culture of that society and none other.[13]

Society, however, as this reference to culture reminds us, is not only a grouping of human beings in various ways, enabling them to live and reproduce their kind in an orderly way. It is also the means by which an heritage of culture is built up, preserved, modified, added to and handed on from generation to generation. In this process the various groups in a society have their particular functions and, in turn, are themselves built up and modified by the culture. Culture is society looked at from its time aspect. It is the accepted way of dealing with the problems of the environment and of life in general, and includes the social, economic, scientific, æsthetic and religious institutions and the intellectual and emotional attitudes which have been adopted and modified and handed down during the society's history—a process which is continuous. Moreover, as the history of any particular society is its *own* history, so its culture, which is an historical process of adaptation, is *peculiar to it.* The society's structure, culture and history constitute a dynamic unity. As a result, a modification of the culture must cause some change in the social structure (that is, the groups and their mutual relations), and, conversely, a change in fundamental social forms such as the family, clan, social ranks or local grouping, brings with it a change in culture and the associated modes of behaviour. In either case, such change causes some alteration in the society's course as set by experience in the past. If the change, whether it originate within or without the society, constitute too great a break with the past, and in the adjustment to the total environment, a social and cultural revolution results, with its consequent disintegration. This may be only temporary, or else so fundamental that cohesion is not recovered. In the case of some peoples, too, depopulation follows. Unless structural and cultural changes can be linked on to the past and accepted by individuals as their own decisions, psychological and sociological disasters ensue.

Such are some of the principles which are established by a study of society and change—which indeed have been revealed by happenings in both the primitive and civilised worlds during the past hundred years. Therefore, seeing in the first place that the contact of civilised peoples with peoples of primitive cultures, through settlers, missionaries and administrators, has caused and must cause such revolutions in the lives of the primitive peoples concerned ; and in the second place that social anthropologists are aware of the consequences which must follow, it is surely their bounden duty to do more than academically analyse the situations and record the results of their investigations. They must also endeavour to constrain the governments, administrations and missionary organisations to accept and act on sociologically determined results

[12] *Vide* A. P. Elkin, *Society, the Individual and Change,* Lecture I, especially pp. 15–30.

[13] *Ibid.,* Lecture II, especially pp. 49–53.

and principles, and at the same time they must proclaim the latter without ceasing to "Everyman", for in the final analysis he is the government, administration and missionary society.

Once again, it is a case of social propaganda, and the specialist must be the propagandist. I have found this to be so with regard to the Aboriginal problem in Australia. In this problem, as in all problems of racial and cultural contact, principles of humanitarianism and justice are evoked, but by themselves are frequently—sometimes correctly—attributed to a sentimentality divorced from knowledge. But a campaign based on sociological analysis of the situation, and on an understanding of the cultures and of the process and effects of change is quite another matter. In a democratic country it must eventually succeed. In this, as in all spheres of human activity, knowledge and understanding must triumph, even against vested interests or indifference. This, of course, is the fundamental reason why the victory of democracy is so essential in the present war.

I therefore suggest that social anthropologists, with the support of those scientific societies which are in a position to evaluate their results, should set themselves the twofold task, first, of disseminating amongst the public generally a knowledge of the established facts and principles regarding native peoples and their cultures and the problem of "racial" contact, and, in the second place, the task of constraining the governments, administrations and missions which are concerned with the Aborigines and the peoples of New Guinea and Papua, always to base their policies and actions on these facts and principles, for sociological science can be applied in such spheres just as chemistry and physics are applied in industry.

Scientific Study of our own Society.

But, as I have implied, what is true of primitive societies is true also of civilised societies, including our own. Structure, culture and history are interrelated, and change is ever upon us, arising from within or without, or both. The immediate cause of such change may be economic, social, political, religious or ethical in nature. Moreover, a change in one sphere will usually cause changes in other spheres. Possibly the greatest and most effective as well as the most disturbing change these days is the phenomenon of war. This is not the reaction of an instinct of pugnacity to an appropriate stimulus. It is the result of an act or a series of acts of decision which are made by a number of persons for the purpose of attaining some desired end or maintaining the *status quo*. But as war is a communal, that is national, effort, the leaders of the nation have to obtain the co-operation of "Everyman", and this means propaganda, whether in democratic or totalitarian countries. While the propaganda may seem to be more thorough or even ruthless in the latter countries, the changes which are wrought in democratic countries by war measures, including propaganda, are relatively greater. We tend, and indeed endeavour, to become in practice totalitarian or at least a planned unit, while at the same time remaining, as far as possible, politically democratic. This implies an important social change, which, if it lasts long, will modify the very structure of our society, made up as it is in no small measure of semi- or almost completely independent groups (employers, investment companies, labour organisations, religious groups, etc.); and such change will have repercussions in the economic, social and political life. Indeed, the very organisation for war inaugurates or accentuates changes which cannot be arrested—changes in the relation of the individual to society, in the position of women, in the balance of the sexes, and in population figures, while war itself raises important problems in the spheres of ethics and

religion.[14] As a consequence of war, the social, economic, political, ethical and religious aspects of a nation's life and structure receive severe shocks : equilibrium is disturbed, and the course of history is altered. In other words, society, which is continually in a process of change, is hurled by a " total " war almost headlong into a vortex of change.

This is vital to us, and hence we hear already of planning for reconstruction after the war—but let us remember that this cannot be reproduction of the pre-war life. If the transition to peace conditions and the building of a " new world " are not to be fraught with disaster, we must do more than think in terms of economics or administration. We must see whether there be any laws revealed in social structure, cohesion and change, and if the sociologists tell us that there are, as they will, then ascertain in what way those laws are functioning in our own society and rest not until schemes of reconstruction take full account of them.

Once again constructive propaganda is required, and social anthropologists and sociologists must be the propagandists. They must show those in authority that they have a practical and essential contribution to make to the ordering, changing and reconstruction of society, and convince the governments that this contribution should be used. At the same time they must disseminate the sociological outlook to " Everyman ", so that it will become natural for those in authority to seek and use the help of this social science whenever important changes are contemplated.

This task will not be easy, for in Australia we have up to the present ignored sociology. There is no chair or lectureship in sociology in any of our universities, though an introduction to it is included in the Anthropology II course at the University of Sydney. But sociology should be provided for in all our universities and secondary schools. Surely it is important to know and understand our own society and our individual relations to it—even though instruction in some other subject has to be omitted : mathematics for some children, Latin or ancient history for others, and so on ! The opinion has recently been expressed by a Cabinet Minister that we should have in this State a university department of rural sociology. I agree, provided that it is associated with a department of sociology in general. May they both be established in the near future !

In this connection it is interesting to notice that while there are only a few university departments of sociology in western Europe, the smaller and " newer " countries in south-eastern Europe seem more willing to accept sociology and to provide it with the opportunity to justify its existence. " Very intense teaching and research in sociology " existed in the former state of Czechoslovakia, where there were three departments of sociology (Prague, Brno and Bratislava). Rumania exhibits an " exceptional understanding for sociology " ; a quite new school of sociological method and thought had been built up in the department of sociology in the Bucharest University, and special attention is paid to rural sociology. Finally, there are six universities and colleges in Yugoslavia in which there are departments of sociology, all recently established.[15] If by chance we are overwhelmed by the great development of sociological teaching and research in America, in schools, colleges and universities, with its various specialisations (urban, rural and Negro), let us look at these small countries, take heart, make a beginning, and go forward.

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[14] On this section, *vide* A. P. Elkin, *Society, The Individual and Change*, Lecture III, especially pp. 70–91.

[15] Nicholas Mirkowich, " Beginnings of Rural Sociology in Yugoslavia ", *Rural Sociology*, Vol. V, No. 3, September, 1940, pp. 351–4.

Science, Education and Everyman.

My theme has been that there are occasions when scientists must be propagandists so as to ensure that their special knowledge is used by the community and its leaders, in peace and war ; and in the refrain after each example I have pointed out that the general public, " Everyman ", as much as the leaders must be the object of this campaigning. Now obviously this would not be necessary if during the years at school every boy and girl (" Everyman " junior) were inspired with the scientific attitude to the problems presented by life, and in simple form with those scientific results which should form the mental stock-in-trade of " Everyman ". Let me enlarge a little : while selected (or self-selected) children will always be encouraged to study one or more scientific subjects (chemistry or other) to the Intermediate or Leaving Certificate standard, all children should be given some idea of the ground covered by the chief scientific disciplines, of the attitude and methods adopted by scientists and finally some idea of the most significant results of each of these sciences for the life of " Everyman ". For example, from the introduction to astronomy could be drawn an appreciation of the concept of order in the universe as well as some understanding of the marvels of the sky, and above all, an inkling, if not a grasp, of the absurdity of astrology ; from physiology could be derived not only enlightenment regarding procreation and its wonder, but also such knowledge regarding illness and disease that the phantasy of Christian science and the shallowness of " medical " quackery will be seen through in advance ; from anthropology could be learnt facts about the human races, nations and cultures which will engender an understanding of, and respect for, other peoples, the facts, too, that war is not inevitable in the sense of springing from man's biological make-up, and that mixed bloods do not *inherit* vices of both their constituent races ; and so on from sociology, psychology, zoology, botany and physics. Of course, the teaching would be graded for primary, intermediate and leaving forms in schools, but if done in an intelligent way would add much knowledge, interest and balance to the life of " Everyman ". Eventually, too, as a result those in authority in the State and in industry would possess the scientific attitude and would know and be expected to know the value of science. Moreover in this way society would be fulfilling its task of handing on to successive generations the results of its experience—not only the experience of trial and error in practical life, but also the experience of the scientist, which is gained through trained observation and the search for natural laws, through experiment and research.

But the imparting of the scientific attitude and the dissemination of scientific knowledge should not terminate with the close of school. The churches do not confine their efforts at indoctrination to the Sunday school, nor the Communists to their youth organisations. Education is a life-long process, and if science is worth while, its specialists should from time to time impart to " Everyman " senior, in as widespread and understandable a manner as possible, the significant results of their special research, as well as a better understanding of the fields and methods of their own branches of science. Finally, as I have tried to show throughout this address, it is their duty to " speak " out when by impartation of their assured knowledge needed warning or help can be given to both government and people alike.

Of course, this contact with " Everyman " implies the co-operation of learned societies, universities, newspapers, publishers and broadcasting commissions and companies. Learned societies, such as our own, and the universities are doing a little by arranging popular lectures. Publishers are for financial reasons naturally hesitant, and so the provision of special publication funds is required. Newspapers and broadcasting authorities could do much more than they do. " Everyman " is really much more intelligent than many

newspapers and broadcast programmes would lead us to believe. Regular articles and talks on their own subjects by specialists with some facility for writing and speaking respectively—in *all* newspapers and over *all* broadcasting networks—would do much good, such articles and lectures to cover all scientific fields, including the social disciplines, and to be concerned with methods and approaches, as well as with descriptions of inventions and processes. In these various ways, during school and adult life, we will eventually reach the stage when we can truthfully speak of a scientific age.

Needless to say, I do not imply that the only scientific research which counts is that which can be seen to bear on definite technical and social problems. Ultimately, no doubt, all scientific research does so bear, but in the meantime scientists will do their research in many cases solely to extend the boundaries of knowledge and to understand better the world and man's relation to it. But even so such knowledge and understanding is for " Everyman "—it belongs to society, and must be woven into its culture. In the long run all knowledge affects living, for knowledge is life, and the scientist is not a miser, hoarding up his knowledge, but one who shares it willingly, though not ostentatiously. It is the welfare of society and the good of " Everyman " which are fundamental, and to that welfare and that good scientists constitute one contributing group, and one of no little value. Its talents must not be hidden, but invested in the life of the nation. And who are the investors ? Surely none other than scientists themselves.

We must remember, however, that science does not provide the only attitude and equipment with which " Everyman " lives or necessarily will live in this world, meeting its problems and experiencing success and failure, joy and sorrow. Science gives knowledge and knowledge power, but our knowledge is still very far from complete and therefore our power is limited. And out of his ignorance and weakness " Everyman " seeks other sources of enlightenment and strength—concerning the validity of which there will be differences of opinion for a long time, perhaps always. Moreover, as Sir James Frazer reminded us at the end of his twelve-volume search for the significance of the " Golden Bough ", " the history of thought should warn us against concluding that because the scientific theory of the world is the best that has yet been formulated, it is necessarily complete and final . . . it may hereafter be superseded by some more perfect hypothesis, perhaps some totally different way of looking at the phenomena, of which we in this generation can form no idea." In the meantime, let scientists be one group which will say to " Everyman "

" I will go with thee
And be thy guide ;
In thy most need
To go by thy side."

THE EFFECT OF THE SYNTHETIC ŒSTROGENS, STILBŒSTROL AND HEXŒSTROL ON THE POUCH AND SCROTUM OF *TRICHOSURUS VULPECULA*.

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(With Plate I.)

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In previous communications[1, 2] it has been shown that the pouch and the scrotum of the common Australian phalanger or possum (*Trichosurus vulpecula*) show marked reactions towards the administration of the esters of naturally occurring œstrogens. In the present communication it will be shown the synthetic œstrogens such as stilbœstrol (4 : 4′ dihydroxy-α, β-diethyl stilbene) and hexœstrol (4 : 4′ dihydroxy-α, β-diethyl dibenzyl), which have no direct chemical relationship to the naturally occurring œstrogens, have a similar action.

(A) The Action of Stilbœstrol and Hexœstrol on the Pouch.

The well developed pouch of *Trichosurus vulpecula* has recently been described.[1] Furthermore, it has been demonstrated that the administration of œstradiol benzoate and œstradiol dipropionate as well as œstrone produce hypertrophy of the muscle situated in the lips of the pouch and secretion of pigment within the pouch. With larger doses a marked contraction of the pouch was produced.

Experimental.

Two fully grown female phalangers were injected with an oily solution of stilbœstrol, three with stilbœstrol dipropionate, and two with hexœstrol. Before injections were begun these animals had pouches of varying sizes, a factor which depended upon whether the animal was in œstrus or had had a young recently. Generally speaking, they all responded to the injections with the different artificial œstrogens in a similar manner. The lips of the pouch became markedly thickened, and the cavity of the pouch decreased in size. The three animals which received the dipropionate of stilbœstrol succumbed with signs and symptoms indicative of renal failure within a fortnight of the commencement of the experiment.[3] The remaining four survived for an indefinite period. Although these animals lost weight during the period of immediate action of the drug, they subsequently increased in size and weight till they were both larger and heavier than at the beginning of the experiment. Three of these experiments will be given in detail.

Experiment S1. The fully grown phalanger weighing 1·9 kg. which was used in this experiment had had a young one approximately a year ago. At the commencement of the experiment (8.8.40) its pouch appeared to be in a state of anœstrus. It was about 1 cm. in depth and practically dry. One day after the injection of 0·9 mg. of stilbœstrol intramuscularly, the lower margin of the pouch was found to be thickened. The right nipple, to which the young had previously been attached, and its mammary gland, appeared to be more prominent than before.

There was also a slight suggestion of moisture in the previously dry pouch. The next day (10.8.40) the depth of the pouch was only about 0·5 cm. The lips were puckered and definitely thickened, particularly caudad. For the next three days similar conditions prevailed. The depth of the pouch became almost negligible and the lips remained thickened and firm. The right mammary gland was now a plaque-like structure of about 1 cm. in diameter and the nipple was definitely larger and firmer when compared with the conditions existing before the experiment began. There was only a slight increase in pigment within the pouch. A week after the injection (15.8.40). the depth of the pouch had increased again to 1·0 cm. and coloured threads of hair provided evidence of pigment secretion on the right nipple. The lips were still thicker than at the commencement of the experiment.

Some days later (20.8.40) another injection of 0·9 mg. of stilbœstrol was given. The response of the pouch seemed to be more marked than after the first injection, and two days after this administration of stilbœstrol the lips were found to be very thick and definite small droplets of fresh pigment were found here and there in the interior of the pouch. The right nipple and mammary gland were very firm. For about ten days the depth of the pouch was decreased as it had been after the first injection, then it increased to about 2·0 cm., but the muscles situated in the lips of the pouch remained prominent. Five weeks after the first injection an intramuscular dose of 1·0 mg. of stilbœstrol dipropionate was given. The effect was essentially the same as that following the administration of free stilbœstrol but seemed to be rather more intense and of slightly longer duration. After its contraction the pouch increased again and about seven weeks after this last injection this organ had a depth of 4·0 cm. This large pouch was found to persist for another three months. The animal itself, after an initial loss of weight of 0·2 kg. during the period of injections, weighed 2·4 kg. at the termination of the experiment. The phalanger, therefore, showed a gain of weight amounting to 0·5 kg. compared with its initial weight.

Experiment S3. The animal used in this experiment was a mature female which about one month previously had lost a pouch young of some 12 cm. in length. Involution of the pouch was incomplete when the experiment began. Its depth was 4·5 cm. and its maximum width 8·0 cm. Some dried pigment was present on the slightly moistened surface of the pouch. An intramuscular injection of 1·5 mg. of stilbœstrol was given (4.9.40). Four and a half hours after the injection the lips of the pouch were taut and the interior was very wet. On the following day the lips were still tense and appeared to be thickened. The depth of the pouch had decreased to 3·5. Five days after the beginning of the experiment (9.9.40) the thickened lips had assumed a cord-like form. At this stage the depth of the pouch was about 3·0 cm. and its maximum width 5·0 cm. On this day a second dose of 1·5 mg. of stilbœstrol was injected. Within the next 24 hours (10.9.40) the pouch became very moist and more pigmented and its depth decreased to 2·5 cm. Two days later (12.9.40) the lips of the pouch were puckered and the depth was only 1·5 cm. On the 13.9.40 it had become about 0·5 cm. deeper. The depth continued to increase during the next few days till it was again 4·5 cm. Another injection of 1·5 mg. stilbœstrol was then given (16.9.40). The subsequent changes in the pouch were essentially the same as those following the earlier injections and a minimum depth of 2·5 cm. was reached three days after this last injection. The pouch then enlarged again and reached a depth of 4·5 cm. two months after the last injection. This large pouch persisted for another two months while the animal was under observation.

At the beginning of the experiment, the animal weighed approximately 2·0 kg. Shortly after the injections had been concluded the animal weighed 1·7 kg. After this it slowly increased in weight and three months after the last injection the animal weighed 2·6 kg.

Experiment S5. This experiment was executed for the purpose of ascertaining if the opening of the pouch moved its position while the pouch itself was undergoing contraction. For this purpose the hairs covering the lower abdomen of a mature female (S5) were removed. Then two straight lines were drawn across the abdomen with silver nitrate at right angles to the long axis of the pouch opening and touching its upper and lower ends. After the lines became visible they were photographed and the animal then was injected with 2 mgm. of stilbœstrol dipropionate (3.10.40). The pouch, which measured only 1·0 cm. in depth before the commencement of the

injection, contracted considerably and was found to measure only 0·3 cm. in depth four days after the administration of the stilbœstrol. The lines drawn with silver nitrate which were originally straight had now become slightly bent in such a fashion that the apex of the curve lay on the mid-line and was pointing cephalad. This seemed to indicate that the lips of the pouch had been pulled cephalad.

(B) The Action of Stilbœstrol and Hexœstrol on the Scrotum.

In a previous communication[2] it has been reported that in immature male phalangers injected with "œstroform" (B.D.H.) brand of œstradiol benzoate, the testes and epididymes leave the prepenile scrotum and become situated under the skin near the inguinal area. This process was called testicular ascent. In older but still sexually immature animals this reaction was slower and less complete, and only after the administration of large and ultimately lethal doses of œstrogens could a complete unilateral ascent be obtained. In sexually mature animals the testes remained confined to the scrotum even after the administration of very large doses of œstrodiol benzoate. However, in one case it was observed that the left testicle, although still completely confined to the scrotal sac, became tightly wedged in the very short scrotal neck.

In the present communication it will be shown that the synthetic œstrogens stilbœstrol and hexœstrol exert a similar action. Observations additional to those already published in connection with the naturally occurring hormones will also be related.

Experimental.

Two sexually mature males and one sexually immature male were injected with stilbœstrol. Four sexually mature specimens were injected with stilbœstrol dipropionate and one with hexœstrol. In all these experiments there was noted a shortening of the scrotal neck. In experiments of sufficient duration and after the administration of a sufficiently large dosage a decrease in size of the testicles as well as the cessation of spermatorrhœa[4] was observed. In the case of a fully grown but sexually immature male (S51) complete bilateral testicular ascent was obtained after injection of stilbœstrol. Subsequently the scrotum reformed, the testicles descended, and spermatozoa appeared in the urine. This particular experiment and another will be given in full detail.

Experiment S51. This experiment was conducted over a period of six months. Before the beginning of the injections the bodyweight of the animal was 2·0 kg. and on the examination of the urine no spermatozoa were observed. Only one urine examination was performed before injections were begun. The testicles appeared to be of about normal size but the neck of the scrotum measured only about 0·5 cm. when extended, giving the scrotum the appearance of a sessile structure. Over a period of three weeks the animal was injected with a total of 4·5 mg. of stilbœstrol averaging about 1·5 mg. per week. After the injections were completed the weight of the animal had decreased to 1·6 kg. It was drinking large amounts of water and it was swollen around the eyes as if œdematous. About three weeks after the cessation of the injection the health of the animal had improved considerably. Its testicles, however, were only about 3/5 of their original size, but the scrotal neck was still very short and practically absent. One month after the last injection it appeared as if the right testicle was beginning to leave the scrotum, and a week later the right testis had completely ascended and became lodged under the abdominal skin, while the left testicle was still in the scrotum. In another week the left testicle had also left the scrotum and was situated under the abdominal skin. At this stage the testes and epididymes appeared to be elongated as compared with their original form, which was almost spherical in appearance. The empty scrotal sac had completely collapsed, forming an area of wrinkled skin flush with the abdominal wall (Fig. 1). Demarcating the scrotal area semi-lunar folds faintly suggesting a rudimentary pouch were sometimes observed. At this stage the

animal weighed 1·9 kg. and appeared to be in reasonably good health. The urine contained no spermatozoa and was also free from casts, which had been noted in previous weeks.

This state of complete testicular ascent persisted for one month. Then the left testicle began to bulge out again into the scrotal skin and a fortnight later the left testis had gone back completely into the scrotum (23.12.40). By this time the right testis began to show signs of imminent descent, which was completed within another week. At this juncture the scrotum formed a sessile structure possessing a maximum diameter of about 4·3 cm. The width of each testis, which was with its epididymis again assuming an almost spherical shape, was about 1·7 cm. The skin of the reformed scrotum was thin and soft like that of a newborn baby.

This status, which was very similar to the one existing before the injections were begun, persisted up to the end of the sixth month of this experiment. Up till then no spermatorrhœa was observed at any time, although the animal must have reached the age of sexual maturity several months previously. On standing the urine took on a dark brown colour as is generally observed to a varying degree in this species. On the hairless skin around the scrotum the secretion of a brown pigment similar to that seen in the pouch of the female was noted. This secretion occurred directly in front of, and particularly behind, the scrotum over a rounded area of about 4 cm. diameter.

In the seventh month of the experiment the appearance of spermatozoa in the urine was noted. At first they did not seem to be numerous and frequently they were deformed, but a few days later they became numerous and with a few exceptions appeared to be normal. On several occasions a few of the spermatozoa were found to be motile. At this stage the weight of the animal was 2·4 kg.

Experiment H50. This animal of 2·3 kg. of bodyweight received injections of 2 mg. of hexœstrol twice a week over a period of four weeks. Spermatorrhœa was present before the injections were begun and persisted during the first two weeks. After this no further spermatozoa were observed in the urine. Before the experiment was begun the scrotal neck measured 5 cm. in length, whilst the maximum diameter of the scrotum was 4·0 cm. Four days after the first injection (8.12.40) the scrotal neck had decreased in length by about 1·0 cm. and after six days this organ had diminished to half its original length. Four weeks after the first injection the scrotal neck had almost completely disappeared and the scrotum became a sessile structure. The testes had considerably diminished in size and consequently the maximum width of the scrotal sac had been reduced to 2·5 cm. After the termination of the injections the maximum diameter of the scrotal sac slightly increased again to 3·0 cm. The scrotal sac appeared to be thickened and had a felt-like texture for a period of about two weeks after the injections had been terminated. During the same period the animal lost weight and its bodyweight diminished to 1·7 kg. The animal remained in this poor condition for about a month, the only change being a lengthening of the scrotal neck to about 2·5 cm. Then it began to increase in weight and three and a half months after the beginning of the experiment the phalanger had reached again its original weight (2·3 kg.), the scrotal neck now measured 4·0 cm. in length, and the maximum diameter of the scrotal sac was also 4·0 cm. (Fig. 3). Spermatozoa reappeared in the urine although in comparatively small numbers. Within another fortnight they became as numerous as they were before the experiment was started.

Discussion.

These experiments indicate that the synthetic œstrogens (stilbœstrol and hexœstrol) act very much like the esters of the naturally occurring œstrogen œstradiol as far as the pouch and the scrotum of *Trichosurus vulpecula* are concerned. Medium and large doses bring on a contraction of the pouch, which is accompanied by hypertrophy and contraction of the pouch muscle. In the male the neck of the scrotum becomes shortened, and in young animals which may be fully grown, though not yet sexually mature, the testes and epididymes may actually leave the scrotum and become situated under the skin near the abdominal ring, while the scrotal sac atrophies.

The present experiments with synthetic œstrogens bring out certain points which enlarge our concept of the action of œstrogens on the phalanger. For example, the marked shortening of the long scrotal neck, which is due to a shortening of cremaster muscle in sexually mature males, though observed, had not been emphasised before. This reaction is undoubtedly similar to that observed in younger animals where actual testicular ascent occurred but where primarily only a very short scrotal neck was present. In the older specimens with a scrotal neck of 4 or more centimetres in length considerable contraction (approx. 4 cm.) has to occur before the testes are close to the abdominal skin as observed in our experiments. On the other hand, in the case of the sessile scrotum of the younger animal, a similar or even a smaller contraction would pull the testicles out of the scrotum and bring them under the skin in front of the abdominal ring.

Similar action should be expected in the case of the *compressor mammæ*, which is the female homologue of the cremaster in the male. This may well be the case, because, when the pouch diminishes in size under the action of the œstrogens, there is also a slight but definite movement of the mammary glands cephalad. For example, in a large pouch the mammary glands are situated practically over the pelvic girdle. In the case of a marked contraction they may be situated near the anterior end of the marsupial bone.

In view of this observation it seems most probable that the cremaster in females (*compressor mammæ*) may undergo a process of shortening as in males and may assist in the contraction of the pouch, which apparently is brought on by all the muscles connected with this organ. Post mortem examination of the cremaster in males and females treated with œstrogens suggests that this muscle has shortened and thickened.

By tracing the distortion of lines drawn on the abdominal wall it has been shown that the pouch opening moves cephalad when the pouch muscles contract. Such a displacement of the opening in relation to the floor of the pouch would increase the depth of the organ. The observed decrease in the depth of the pouch cannot to any extent be accounted for by changes in the relative positions of the opening and the floor except in so far as the floor moves cephalad to a greater degree than does the opening.

In addition to this conception of œstrogenic action on the cremaster of males and females several other points became more clearly defined in the course of this present study. Previously testicular ascent had been produced by persistent administration of œstrogens, and with the exception of a very young male that had small but numerous injections all the animals died as a result of the experiments. The fate of the ascended testes following cessation of the treatment was, therefore, not observed. In the present investigation it was noted that some time after the administration of the drugs was suspended the testicles returned to the scrotum. These observations are another example of the antagonism between œstrogenic substances and the male sex hormone, testosterone. The former cause shortening of the scrotal neck with contraction of the cremaster muscle, while testosterone produces an elongation of the scrotum associated with lengthening of the cremaster.[5]

All the animals treated lost weight while the injections were given and for some time afterwards. This, in part, may have been due to the renal insufficiency produced in these animals and not due to the growth-hindering action of œstrogens. However, those animals which survived for one month after the injections had ceased not only made up the weight lost previously, but they all became heavier than they were before the injections were begun. This group of animals was definitely heavier than a control group of similar phalangers which was kept in the laboratory on the same diet for a similar time. It is realised

that the group of animals under discussion is rather a small one ; notwithstanding this fact, these animals treated with stilbœstrol and hexœstrol did not exhibit any growth-inhibiting reaction, but on the contrary their growth has, if anything, been stimulated by these hormones.

The increase of pigment in the pouch was less pronounced than in experiments with natural œstrogens. In spite of frequent association with males none of the female phalangers which had been injected with artificial œstrogens has subsequently become pregnant. Restoration of spermatogenesis in the males was shown by the reappearance of spermatozoa in the urine.

Summary.

In the female of *Trichosurus vulpecula* stilbœstrol and hexœstrol produced hypertrophy of the pouch muscle and contraction of the pouch.

In the male, cessation of spermatorrhœa, shortening of the neck of the scrotum, and decrease in size of the testicles are the most obvious reactions, but all of them are reversible. In the younger animals testicular ascent occurs, and in one experiment on an apparently fully grown, though sexually immature male, complete testicular ascent was obtained. Some time after the injections were terminated the testicles descended again into the scrotum and became of normal size. This was accompanied by restoration of spermatogenesis.

These findings, which are similar to those observed after the administration of esters of œstradiol, have been discussed, and the shortening of the cremaster of males and females has been recognised as a manifestation of œstrogenic activity.

Acknowledgment.

The authors wish to thank Mr. G. K. Hughes for preparing the hexœstrol used in this investigation.

References.

(1) Bolliger, A., and Carrodus, A.: This Journal, 1940, *73*, 218.
(2) Bolliger, A., and Carrodus, A.: *Austral. New Zealand Journ. Surg.*, 1939, *9*, 155.
(3) Bolliger, A., and Canny, A. J.: *Med. Journ. Austral.*, 1941, 697.
(4) Bolliger, A., and Carrodus, A.: *Med. Journ. Austral.*, 1938, 1118.
(5) Bolliger, A., and Carrodus, A.: *Med. Journ. Austral.*, 1940, 368.

Description of Plate I.

Fig. 1.—Experiment S51. Complete testicular ascent three months after beginning injections with stilbœstrol. Note the collapsed scrotal sac and the elevations on the abdominal skin lateral to it indicating the new positions of the testicles.

Fig. 2.—Experiment S51. Redescended testes five and a half months after beginning the injections with stilbœstrol. Note the thinness of the scrotal sac.

Fig. 3.—Experiment H50. Three months after cessation of hexœstrol injections the scrotal neck has been restored to its previous length. At this stage the appearance of the scrotum is the same as before the experiment commenced. The scrotum had to be held in this extended position to prevent voluntary retraction.

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Fig. 1

Fig. 2

Fig. 3

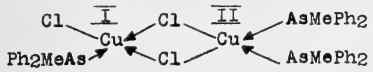
MAGNETIC STUDIES OF COORDINATION COMPOUNDS.

Part V. Binuclear Copper Derivatives of Diphenyl Methyl Arsine.

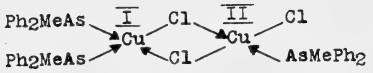
By D. P. Mellor, M.Sc.,
and D. P. Craig, B.Sc.

(*Manuscript received, April 21, 1941. Read, May 7, 1941.*)

In order to explain the isomerism of two copper derivatives of diphenyl methyl arsine, first described by Burrows and Sanford,[1] the following structures have been proposed.[2]



I.



II.

The isomerism depends essentially upon the difference in stereochemical properties of cuprous (Cu^{I}) and cupric (Cu^{II}) copper. Four covalent bonds to Cu^{I} are always tetrahedrally arranged as in CuCl. Quadricovalent Cu^{II}, on the other hand, is characterised by square coordination, as in $CuCl_2 2H_2O$. There is no reason to believe that cupric copper forms other than predominantly covalent bonds in (I) and (II), since the extent of the covalent character of the bonds is determined largely by the electronegativity of the atoms attached to the metal. As arsenic is less electronegative than oxygen, the conditions for forming covalent bonds with Cu^{II} in (I) and (II) are just as favourable as in $CuCl_2 2H_2O$. Up to the present, the main evidence for the existence of copper in the two valency states in the above compounds has rested upon chemical analysis: the composition of each form corresponds to the empirical formula $Cu_2Cl_3(Ph_2MeAs)_3$. On account of its significance in regard to the constitution of these compounds it was thought worth while to check the existence of the two valency states by means of magnetic measurements. A satisfactory check of this kind will not, of course, prove the correctness of the proposed structures in the way that a complete X-ray crystal analysis would. Because, however, it is very unlikely that complete analyses of such complicated structures will be carried out for some time to come, the most promising line of attack on the constitution of these compounds lies in the accumulation of as much indirect evidence as possible.

The magnetic properties of copper compounds which have been extensively studied by Sugden may be summarised as follows: Cuprous compounds are diamagnetic, a fact which is taken to mean that the cuprous atom contains no unpaired electrons. Cupric compounds on the other hand are always paramagnetic, with moments ranging between 1·7 and 1·9 Bohr magnetons, that is, the cupric atom contains one unpaired electron. Thus if formulæ I and II are correct, each molecule should contain one unpaired electron.

Experimental.

The main objects of these additional notes on the preparation of the compounds are (1) to draw attention to certain significant colour changes which occur in the course of the preparations,

and (2) to specify more definitely the conditions for obtaining the blue form free from the brown. To make the brown form, diphenyl methyl arsine (1 mol.) was slowly added to an alcoholic solution of cupric chloride (1 mol.). The dark brown colour of the alcoholic cupric chloride solution slowly disappeared owing to the almost complete reduction of the cupric ion. On allowing the solution to stand about 12 hours the brown colour reappeared, owing to aerial oxidation of some, at least, of the cuprous copper.

To make the blue form, cupric chloride dihydrate (1 mol. 12·2 gm.) was dissolved in 50 ml. of boiling alcohol and diphenyl methyl arsine (1 mol. 17·5 gm.) was then added drop by drop over ten minutes. The resulting pale brown solution was kept between 50° and 60° for 45 minutes. Sufficient aqueous alcohol (2 parts alcohol : 5 of water) was then added to bring the total volume of the solution up to 800 ml. This volume of aqueous alcohol was found to be sufficient to hold up the white cuprous compound ($CuPh_2MeAsCl$). At this stage the solution was *water white*. If air were excluded from it no colour change occurred, but on allowing the solution to come freely into contact with the air it slowly developed a blue colour closely resembling that of cupric sulphate, and, after about 24 hours, crystals of the blue form began to separate. Once again the marked colour change indicates aerial oxidation of part, at least, of the cuprous copper. Chemical analysis and magnetic measurements show that only part of the cuprous copper is oxidised.

As already pointed out,[2] both forms can be recrystallised from nitrobenzene. The appearance of the blue form when recrystallised from nitrobenzene is somewhat altered. Instead of being a sky blue it takes on a more greenish hue, presumably because it separates in smaller crystals. Examination of the pleochroism of the two sets of crystals under a polarising microscope and chemical analysis show that they are the same substance.

Since the compounds were previously analysed for Cu, Cl and As only, it was decided to check and extend the analyses to all constituents. The following results were obtained :

	Cu	Cl	As	C	H
	%	%	%	%	%
Blue form* (from aqueous alcohol)	13·9	10·5	22·1	45·1	4·1
Blue form* (from nitrobenzene)	13·8	10·5	22·0	44·7	4·0
Blue form†	13·1	10·8	22·1	—	—
Brown form*	13·9	10·6	22·3	44·9	3·9
Brown form†	13·2	10·9	22·6	—	—

There is no doubt that the two forms have the same composition.‡ This evidence, in conjunction with molecular weight determinations, makes it clear that the two compounds are isomeric. The low results for carbon are very puzzling and as yet no explanation for them can be suggested. One possibility that suggested itself, but which was finally excluded, was that an arsine oxide might have been formed and coordinated with copper. Residues left after the separation of crystals of both the blue and brown forms invariably yielded, on long standing, flaky white crystals of $(C_6H_5)_2CH_3AsO$.

This substance, if present in the copper complexes, could account for low carbon. There is, however, no evidence that it is present. On passing dry ammonia over the blue and brown

* Microanalyses carried out by Dr. G. Burger of the University of Adelaide.

† Analysis by Burrows and Sanford.

Calculated for $Cu_2Cl_3(Ph_2MeAs)_3$: Cu=13·1%, Cl=10·9%, As=23·3%, H=4·0%, C=48·8%.

‡ In order to test whether the blue form is a hydrate of the brown, weighed amounts of the blue form both in the coarsely crystalline and very finely powdered form were exposed over P_2O_5 *in vacuo* for two weeks. At the end of this time, although the finely powdered sample had become brown, no change in weight could be detected.

copper complexes it was slowly absorbed with the simultaneous expulsion of the arsine, which on account of its low volatility remained with the copper ammonia complex formed. By treating the residue (from the ammonia treatment) with methyl iodide and then extracting with ether, the arsine could be recovered as the methiodide.*

Magnetic Measurements.

Although a fairly large tube was employed in these measurements, the change in weight of the substance due to the magnetic field was rather small on account of the large diamagnetic contribution of the molecule. Because of this the accuracy of the measurements is not high. As a check on the measurements, copper phthalocyanine, a substance which also has a high molecular weight and hence a large diamagnetic contribution, was measured. Its moment was found to be 1·72 Bohr magnetons, a value which agrees very well with that obtained by Klemm[3](1·73). As a matter of interest, measurements were also made on the complex copper cyanide $Cu_3(CN_4)(NH_3)_3$,[4] the molecule of which should contain one unpaired electron. The experimental results are summarised in Table 1.

TABLE 1.

Substance.	Molar Susceptibility. $\chi_M^{25} \times 10^6$	Magnetic Moment μ (Bohr Magnetons).
1. Copper phthalocyanine	890	1·72
2. $Cu_2Cl_3(Ph_2MeAs)_3$ (blue)	830	1·79–(1·5)
3. $Cu_2Cl_3(Ph_2MeAs)_3$ (brown)	812	1·78
4. $Cu_3(CN)_4(NH_3)_3$	1195	1·78

Some specimens of the blue form gave low results for the magnetic moment ($\mu = 1·5$) but no satisfactory explanation could be found for these figures. The higher value quoted in the table refers to a specimen recrystallised from nitrobenzene. Magnetic moments were calculated on the assumption that the compounds followed Curie's Law. The following calculated diamagnetic corrections ($\times 10^6$) were used: 1.–338, 2.–515, 3.–515, 4.–125.

DISCUSSION.

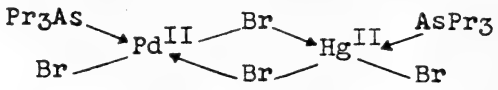
It can be seen that the results of the magnetic measurements are consistent with the formulations I and II for the two isomers, but further work will be needed before these constitutions can be considered as established. So far, all attempts to elucidate the structures by experiments on the fission of the binuclear complexes with various reagents have failed.

The transformation of one isomeric form to the other, which takes place fairly readily, can be pictured as occurring in a very simple way—namely, by the transfer of an electron from the Cu^I to Cu^{II}. This transfer would be accompanied by such changes in bond orientation about the copper atoms as would be determined by their new valency states.

It is interesting to note that Mann and Purdie[5] have recently described a compound very similar to (I) and (II). The compound, dibromobistripropyl arsine-u-dibromopalladium mercury (III) is similar in the sense that it contains two metal atoms about which four covalent bonds are directed to the corners of a square and a tetrahedron respectively. The similarity extends to the fact that (III), like (I) and (II), undergoes dissociation in solution, but an important

* Unpublished experiments with B. S. Morris.

difference arises in regard to the possibilities of isomerism. Isomerism of the type observed with the copper compounds cannot occur with (III). This is related to the fact that in the former the two metal atoms are uni- and bivalent respectively, whereas in the latter both metal atoms are bivalent.



III.

SUMMARY.

Magnetic measurements show that the molecule of each form of $Cu_2Cl_3(Ph_2MeAs)_3$ contains one unpaired electron. This is consistent with the structures previously proposed for these isomers.

REFERENCES.

(1) G. J. Burrows and E. P. Sanford: THIS JOURAL, 1935, *79*, 182.
(2) D. P. Mellor, G. J. Burrows and B. S. Morris: *Nature*, 1938, *141*, 414.
(3) W. Klemm and L. Klemm: *Journ. für prakt. Chem. N.F.*, 1935, *143*, 82.
(4) Treadwell and Girsewald: *Zeit. für anorg. Chem.*, 1904, *39*, 84.
(5) F. D. Mann and D. Purdie: *Journ. Chem. Soc.*, 1940, 1230.

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PROGRESSIVE RATES OF TAX IN AUSTRALIA.

By H. S. Carslaw, Sc.D., LL.D.

(With 15 text-figures.)

(*Manuscript received, March 25, 1941. Read, May 7, 1941.*

Introductory.

Heavy expenditure on war purposes has made the Federal Government obtain from income tax a much larger revenue. As the State taxes on income are far from uniform, and the Federal tax must be the same throughout Australia, the Federal authorities are seriously hampered at all points of the scale, and not least in their dealings with high incomes. It seems clear that the present position with regard to taxation of incomes cannot continue.

Both Federal and State Income Tax Schedules are based upon a progressive rate of tax whose principle is little understood. It may be helpful in present circumstances to give a simple and critical exposition of the system and of its use by Federal and State authorities. Only elementary mathematics is employed, but with the aid of mathematics a little more advanced the matter could be put more concisely and naturally.

Progressive Rates in Federal Taxes.

1. The simplest form of tax is that in which the rate is constant; e.g. 6 pence in the £. Next comes a graduated tax of which the following may be taken as an example:

On so much of the Income as	The Rate of Tax per £ shall be
	s. d.
Does not exceed £500	0 6
Exceeds £500 but does not exceed £1,000	0 8
Exceeds £1,000 but does not exceed £1,500	0 10
Exceeds £1,500 but does not exceed £2,000	1 0
Exceeds £2,000	1 2

Let the amount of the tax on an income of £x be T pence.

Then $T=6x$, when $0<x\leqslant 500$.

$T=6\times 500+8(x-500)$, when $500<x\leqslant 1000$.

$=8x-1000$.

$T=6\times 500+8\times 500+10(x-1000)$, when $1000<x\leqslant 1500$.

$=10x-3000$.

$T=12x-6000$, when $1500<x\leqslant 2000$.

and $T=14x-10{,}000$, when $2000<x$.

The amount of the tax on an income of £x can be read off from Fig. 1, by finding the area between the axis of y, the "step" function, the ordinate at x and the axis of x.

Now bisect the segments in Fig. 1. It will be seen that the middle points lie on the line whose equation is

$$y=\frac{x}{250}+5 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

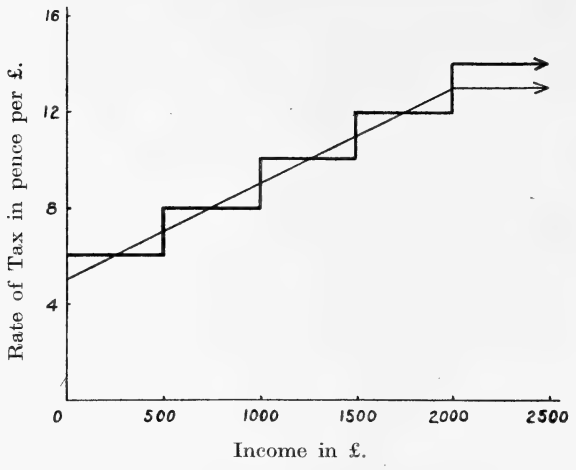


Fig. 1.

Referring to Fig. 2 and raising the ordinates at $x=50$, 150, 250, etc., to this line, we see that a graduated tax in which steps of 2/5ths of a penny take place at intervals of £100, while the amount of the tax on incomes of £500, £1,000, £1,500 and £2,000 is the same as before, is as follows :

On the 1st £100 there will be a flat rate of $(5+1/5)$ pence ;
on the 2nd £100 of $(5+3/5)$ pence ;
on the 3rd £100 of $(5+1)$ pence,

and so on, till on the 20th £100 there will be a flat rate of $\left(5+\frac{2\times 20-1}{5}\right)=\left(13-\frac{1}{5}\right)$ pence. In this case it would be natural on the excess over £2,000 to make the flat rate 13 pence in the £.

Also, if we carry the steps down to intervals of £1, we obtain again from the line (1) the following scheme :

On the 1st £ the amount of the tax will be $(5+1/500)$ pence ;
on the 2nd £, $(5+3/500)$ pence ;
on the 3rd £, $(5+5/500)$ pence ;

and so on.

The amount of the tax on the nth £ will be $\left(5+\frac{2n-1}{500}\right)$ pence, and on the 2,000th £ it will be $(13-1/500)$ pence.

With this graduated tax it would be still more natural to have a flat rate of 13 pence in the £ on the excess over £2,000.

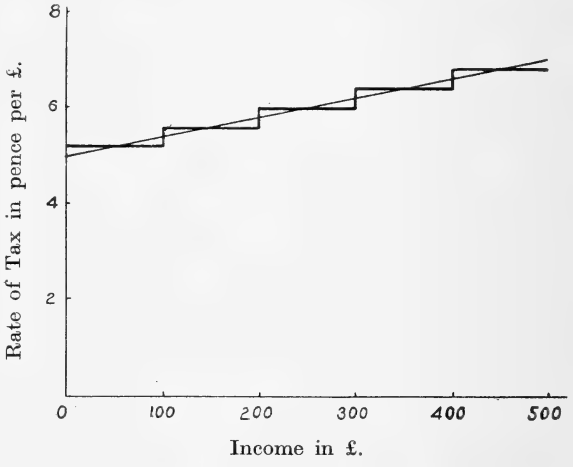


Fig. 2.

Then, with the above notation, on summing this arithmetical progression,

$$T=x\left(\frac{x}{500}+5\right),$$ when x is any positive integer not exceeding 2,000

and $$T=13x-8000,$$ when x is greater than 2,000.

2. On the other hand, if we start with a formula of the type

$$T=x(ax+b)$$

and subtract the tax on an income of £$(x-1)$ from that on an income of £x, we see that the xth £ pays

$$x(ax+b)-(x-1)[a(x-1)+b] \text{ pence,}$$

i.e., $a(2x-1)+b$ pence.

Thus the 1st £ pays $(a+b)$ pence,
the 2nd £ pays $(3a+b)$ pence,
the 3rd £ pays $(5a+b)$ pence,
and so on, the amounts paid by each successive £ forming an arithmetical progression whose first term is $(a+b)$ and common difference $2a$.

Writing $T/x=R$, it is usual in Australia to call R the rate of tax for every £ of the income of £x.

Thus, when $R=ax+b$, the amount paid by each successive £ exceeds that paid by the preceding £ by $2a$ pence.

A progression of this sort must stop at some figure or too much would be taken from each additional £ of the income. If it stops, say, at £5,000, and there is a flat rate on the excess over £5,000, it would obviously be wrong to make each £ of the excess pay less than that paid by the 5,000th £. From the mathematical point of view it would be right to take "the rate *at* x_0" for the flat rate on the excess over £x_0. "The rate *at* x_0" is $2ax_0+b$ and can be found by reducing the steps from intervals of £1 to gradually smaller and smaller intervals.

The progressive rate, when R is of the form $ax+b$ up to a certain value of x, and there is a suitably chosen flat rate on the excess over that sum, is a natural extension of the simple graduated tax, where steps of the same size are taken at equal intervals, say of £100, up to a certain sum and there is a flat rate on the excess.

3. There is a simple graphical representation of the amount of the tax on an income of £x, when $T=x(ax+b)$.

In Fig. 3, $OM=x$, $OH=MK=b$, $KQ=ax=QP$.

Then HQ is the line $y=ax+b$ and HP is the line $y=2ax+b$.

The area of the rectangle $OMQN$ is $x(ax+b)$ and the area of the trapezium $OMPH$ is the same as that of the rectangle.

Thus the line $y=2ax+b$, by means of the area $OMPH$, provides a representation of the tax payable when the rate R is $ax+b$.[1] Also, the tax on the xth £ is given by the area of the trapezium $M'MPP'$, where $OM=x$ and $OM'=(x-1)$, namely $[a(2x-1)+b]$.

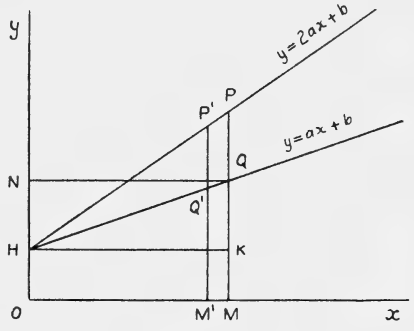


Fig. 3.

If a is small, this tax is approximately $2ax+b$ and is represented by the ordinate at x to the line $2ax+b$.

In Fig. 4 the line P_0P_1 is drawn through P_0 parallel to the axis of x. The area between this line HP_0P_1, the ordinate at any point, and the axes, represents the amount of the tax, when the rate R is $ax+b$ up to £x_0 and there is a flat rate of $2ax_0+b$ in the £ on the excess over £x_0.

If the flat rate on the excess is c instead of $2ax_0+b$, we have to use the line $y=c$ in the diagram instead of the line $y=2ax_0+b$.

4. In §3 we reached the flat rate by only one progression. It would be natural to introduce another in the range from £x_0 to £x, with a smaller common difference, and perhaps even another, with the flat rate to follow.

[1] I am indebted to a referee for this way of evading the Calculus.

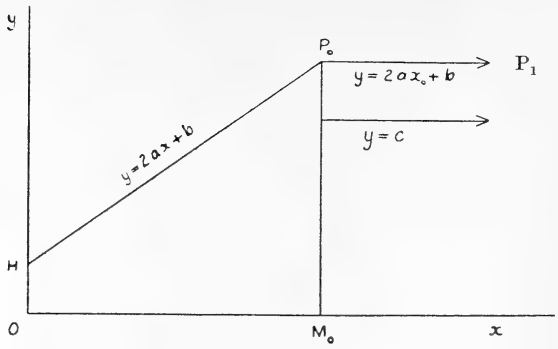


Fig. 4.

Such a system is illustrated in Fig. 5, where it will be noticed that the line $HP_0P_1P_2$ is continuous, and this requires that

$$2ax_0+b=2a'x_0+b'.$$

The 1st £ pays $(a+b)$ pence
„ 2nd £ pays $(3a+b)$ pence
„ 3rd £ pays $(5a+b)$ pence
. . .
and the x_0th £ pays $[a(2x_0-1)+b]$ pence. } Common difference $2a$.

Then the (x_0+1)th £ pays $[a'(2x_0+1)+b']$ pence[2]
the (x_0+2)th £ pays $[a'(2x_0+3)+b']$ pence
and the x_1th £ pays $[a'(2x_1-1)+b']$ pence. } Common difference $2a'$.

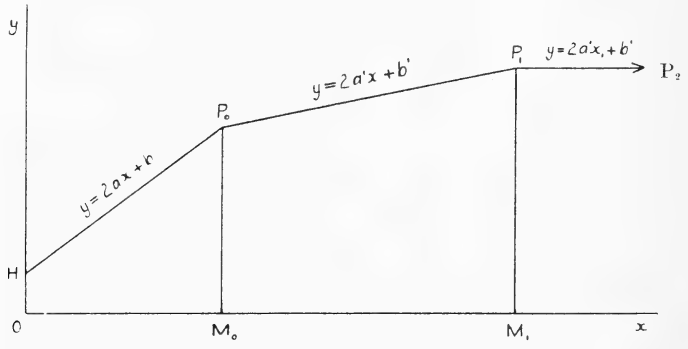


Fig. 5.

There is a flat rate $2a'x_1+b'$ on the excess over £x_1. It will be seen that the amount of the tax on an income of £x is given by the area bounded by the line $HP_0P_1P_2$, the ordinate at x, and the axes.

When $0<x\leqslant x_0$, $T=x(ax+b)$.

When $x_0<x\leqslant x_1$, $T=x(a'x+b')+x_0\{ax_0+b-a'x_0-b'\}$.

$$=x(a'x+b')+\tfrac{1}{2}(b-b')x_0,$$

since $2x_0(a-a')=(b'-b)$.

5. One other remark is required before concluding this theoretical section. With the line $y=2ax+b$ in the first interval, it might seem proper to take the line $y=2a'x+b'$ in the next interval from x_0 to x_1, making $ax_0+b=a'x_0+b'$, with a' less than a.

[2] This is $(a+a')$ pence more than the x_0th £ pays.

But, if $ax_0+b=a'x_0+b'$, and a' is less than a, the line $y=2a'x+b'$ cuts the ordinate at x_0 as in Fig. 6, and there is a jump down at x_0 in the amount paid by the (x_0+1)th £.

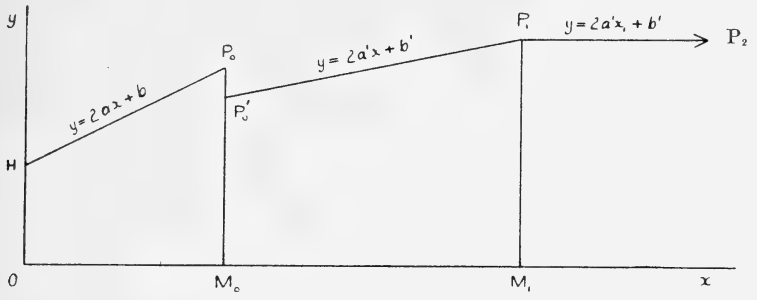


Fig. 6.

It will be seen that $P_0'P_0=(a-a')x_0$ and that this jump down may be considerable.

However, with Fig. 6,

When $0<x\leqslant x_0$, $T=x(ax+b)$;

and when $x_0<x\leqslant x_1$, $T=x(a'x+b')+x_0\{ax_0+b-a'x_0-b'\}$

$=x(a'x+b')$,

since $ax_0+b=a'x_0+b'$.

The fact that T in the second interval, when $ax_0+b=a'x_0+b'$, takes the simple form $x(a'x+b')$ seems to have tempted the Federal and some of the State authorities to adopt this system instead of that described in §4.

It will be seen later how seriously this affects the continuous progression in the amounts paid by the successive £'s. There can be no question that the jumps made in these cases are as inequitable as making the final flat rate different from that indicated by the amount paid on the last £ of the progression.

6. A progressive rate, where each successive £ pays just a little more than the preceding up to a certain stage and there is a flat rate on the excess, determined by the amount which the last £ of the progression pays, was used for the first time in taxation when the Commonwealth of Australia in the financial year 1910-11, began its Land Tax. The formula was due to Sir George Knibbs, the first Federal Statistician. Residents in Australia were allowed an exemption of £5,000. In their case the taxable value of their land was the actual value less £5,000.

Particulars of the tax are given in the following table.[3]

LAND TAX. RATE OF TAX PER £ OF TAXABLE VALUE.
($£x$=Taxable Value.)
Residents.

Assessment Year.	Taxable Value £1 to £75,000.	Taxable Value over £75,000.	
		First £75,000.	Excess over £75,000.
1910-11 to 1913-14	$\left(1+\frac{x}{30,000}\right)$ d.	d. 3·5	d. 6
1914-15	$\left(1+\frac{x}{18,750}\right)$ d.	5	9

[3] Official Year Book of the Commonwealth of Australia, No. 32, p. 836 (1939).

Absentees.[4]

Assessment Year.	Taxable Value £1 to £80,000.		Taxable Value over £80,000.		
	First £5,000.	Excess over £5,000.	First £5,000.	Next £75,000.	Excess over £80,000.
1910-11 to 1913-14	d. 1	$\left(2+\frac{x-5,000}{30,000}\right)$ d.	d. 1	d. 4·5	d. 7
1914-15	1	$\left(2+\frac{x-5,000}{18,750}\right)$ d.	1	6	10

The rates for 1914-15 have been the basic rates since that year, altered from time to time by certain percentages. It will be noticed that, when the progression ends, the flat rate on the excess is determined by the amount paid on the last £ of the progression.

7. The Federal Government first imposed an income tax in the financial year 1915-16. For earned income the rate of tax was of the same type as in the land tax for residents.

With the notation of this paper, in the 1915 Act the scale is given by the formula :

When $0<x\leqslant 7,600$, $R=3+\frac{3x}{800}$;

When $7,600<x$, on the first £7,600, $R=3+\frac{3\times 7,600}{800}=31\cdot 5$,

and on the excess over £7,600 the rate of tax per £ is 60 pence.

In Fig. 7 we have a graphical representation of this tax.

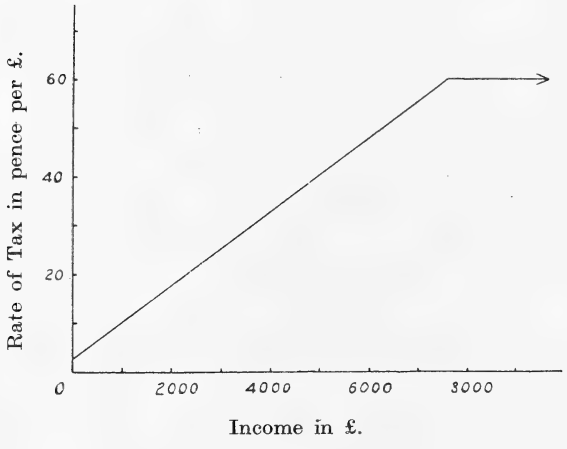


Fig. 7.

The area between the line $y=3+\frac{3x}{400}$, $0<x\leqslant 7,600$ and $y=60$, $x>7,600$ the axes of x and y, and the ordinate at any point x, represents the amount of the tax on an income of £x; and the tax on the xth £, when x does not exceed 7,600, is given by the ordinate at x less 3/800.

From §2 we know that the 1st £ pays (3+3/800) pence, the 2nd £ (3+9/800) pence, the 3rd £ (3+15/800) pence, and so on, these amounts forming an arithmetical progression with common difference 3/400. The 7,600th £ pays (60−3/800) pence and every £ of the excess pays 60 pence.

[4] Absentees are not allowed an exemption.

Unfortunately, in dealing with property income, Knibbs introduced complexities of a mathematical kind.[5] For the first £546 of taxable income, the formula for R was of a type similar to that for earned income; the amounts paid by each successive £ formed an arithmetical progression. From £546 to £2,000 each successive £ paid just a little more than the preceding £, but the progression was not arithmetical. Here his "curve of the second degree" entered. From £2,000 to £6,500 each successive £ paid just a little more than the preceding. Here his "curve of the third degree" came in. Every £ of the excess over £6,500 paid 60 pence, this being the amount paid by the 6,500th £.

There seems no doubt that Knibbs could have got all he needed by breaking up the interval into three parts, in each of which a different arithmetical progression was used, as described in §4.

A ready reckoner was issued by the taxation authorities showing the amount of the tax on any income. Without its help the taxpayer would have been quite ignorant of what he had to pay.

When income was derived partly from personal exertion and partly from property, the rate on the earned income was that for an earned income of the whole amount, and that on the property income also that for a property income of the whole amount. This principle is to be understood as applying below to both State and Federal incomes of this kind unless otherwise remarked.

8. These rates of tax remained the basic rates for Federal income tax from 1915-16 till 1930-31. They were altered from time to time by certain percentages, sometimes over the whole income range, sometimes only over parts of the range. For some years there was a Special Property Tax at a flat rate. In this way the gradual progressions of the original formulæ were interfered with; and for this as well as other reasons a new scale of rates was devised for the year 1931-32. The person responsible on that occasion was Professor Giblin. Knibbs's curves were dropped. The Integral Calculus had no longer to be used in determining the amount of the tax. The linear rate $R=ax+b$ remained the characteristic feature of the formulæ for both kinds of income.

The new scales can be stated as follows:

Earned Income.

(i) If the taxable income does not exceed £6,900, $R=3+\frac{x}{160}$.

(ii) If the taxable income exceeds £6,900,

on the first £6,900, $R=3+\frac{6,900}{160}=46\cdot125$, and on the excess over £6,900 the rate of tax per £ is 90d.

Property Income.

(i) If the taxable income does not exceed £500, $R=3+\frac{x}{100}$.

(ii) If the taxable income exceeds £500 but does not exceed £1,500, $R=1+\frac{14x}{1,000}$.

(iii) If the taxable income exceeds £1,500 but does not exceed £3,700, $R=4\frac{3}{4}+\frac{23x}{2,000}$.

(iv) If the taxable income exceeds £3,700, on the first £3,700, $R=4\frac{3}{4}+\frac{23\times3,700}{2,000}=47\cdot3$,

and on the excess over £3,700 the rate of tax per £ is 90d.

[5] For these, reference can be made to a paper by Carslaw in *The Economic Record*, Vol. 7 (1931), entitled "The Federal Income Tax Acts, 1915-1931".

These scales[6] are represented on Fig. 8. That for earned income is the familiar type with the amounts paid by each successive £ up to the 6,900th forming an arithmetical progression with a common difference 0·0125 d. The flat rate on the excess is determined by the amount paid on the last £ of the progression.

In the scale for property income it will be noticed that R is continuous at £500 and £1,500. The discussion in §5, though given for the case of only two intervals, applies also to any number. The gradient in the interval 500 to 1,500 is steeper than that in the interval 1 to 500. This explains the jump up at 500 in the amounts paid by the adjacent £'s and the formulæ (i) and (ii) show that this is as much as 2d., whereas the common difference in the progression from 1 to 500 is 0·02, while that in the interval 500 to 1,500 is 0·028. Again at 1,500 there is a jump down of nearly 4d.

These awkward breaks at the 500th £ and at the 1,500th are a blot on this scale. Indeed it is surprising that it was allowed to remain the basic rate from 1931-32 till 1939-40, with percentage changes over the whole range from time to time as the revenue needs demanded more or less.

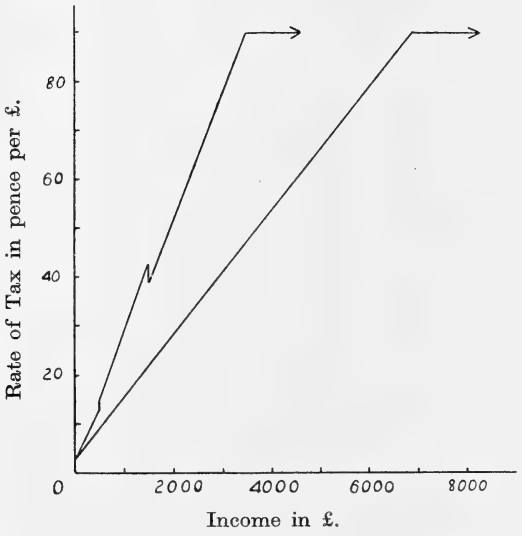


Fig. 8.

It is also rather astonishing that a simpler means of discriminating between the two kinds of income has not even yet been adopted by the Federal authorities. There is much to be said in favour of the method used in England. A certain proportion is deducted from the total of the earned income, but this deduction must not exceed a certain sum. When the earned income has been reduced in this way and the deductions, as provided in the regulations, have been made from each class of income, the two are treated alike; their sum forms the taxable income and the rates of tax refer to the taxable income without any further distinction as to the way in which it is composed.

9. For the year 1939-40 the Federal Parliament passed two Income Tax Acts. The Income Tax Act (No. 1) 1940, of May, anticipated the budget for the year, which was placed before the new Parliament in November. The Federal Treasurer, then Mr. Spender, in introducing the measure, made some reference to the "income tax technique" adopted by the Commonwealth and the rates of tax designed by Sir George Knibbs. He was bold enough to assert[7] that "for some considerable time the Commonwealth led the world on methods of income taxation and other countries followed. In particular, most of the Australian States followed the Commonwealth lead, improved on the principle, and adapted it to their own needs." This praise seems to me somewhat excessive

[6] In Fig. 8 and later figures, the upper of the two graphs refers to Property Income.

[7] Commonwealth of Australia, Parliamentary Debates, 15th Parliament, 2nd Session, p. 604 (1940).

and with regard to the so-called improvements the States made on the principle there will be something to say later.

The scheme embodied in Schedules I and II of the Income Tax Act (No. 1) 1940 was influenced by the incidence of the State taxes on income. "This practical limitation of Federal income taxation", said the Treasurer,[8] "causes difficulties at present, but not of a serious order." Six months later his successor, Mr. Fadden, had a different tale to tell.

The scale of rates can be put briefly as follows:

Earned Income.

When $0<x\leqslant 500$, $R=5$.

„ $500<x\leqslant 1{,}000$, $R=\frac{x}{50}-5$.

„ $1{,}000<x\leqslant 4{,}200$, $R=\frac{x}{100}+5$.

„ $4{,}200<x$, on the first £4,200, $R=47$, and on the excess over £4,200 the rate of tax per £ is 90 pence.

Property Income.

When $0<x\leqslant 500$, $R=6$.

„ $500<x\leqslant 1{,}000$, $R=\frac{3x}{100}-9$.

When $1{,}000<x\leqslant 4{,}200$,

$$R=\frac{x}{80}+8\tfrac{1}{2}.$$

„ $4{,}200<x$, on the first £4,200, $R=61$,

and on the excess over £4,200 the rate of tax per £ is 108 pence.

These scales are represented in Fig. 9. They are again examples of the system discussed in §5, R being continuous in both at 500 and 1,500. There are extremely awkward jumps at these points, and, while the flat rate on the excess over £4,200 in earned income does not differ much from that indicated by the amount the last £ of the progression pays, in the case of property income it is chosen as 108 pence per £ instead of 113·5.

The defects in these scales are so serious that one wonders how the committee of experts, with Professor Giblin as economic adviser, came to recommend them to the Federal Treasurer.

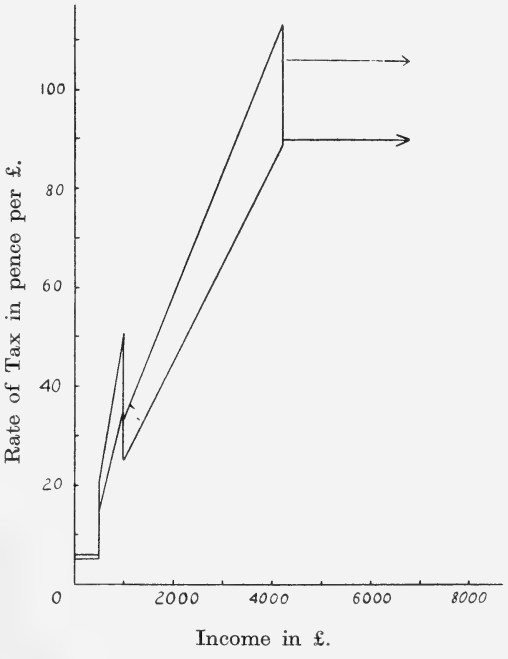


Fig. 9.

10. However, when the budget for the year 1939-40 was put before Parliament at the end of November, the increased war expenditure required that income tax provide a much greater revenue, and the Acts passed in May

[8] *Loc. cit.*, p. 606.

dealing with assessment and rates had to be replaced by others. The statutory exemption, about which nothing has been said so far in this paper, since 1931-32 had been £250, diminishing by £1 for every £2 by which the net income exceeded £250, and thus vanishing at £750. In the Assessment Act (No. 1) 1940 this had been replaced by £250, vanishing at £500. When Mr. Fadden introduced the new Assessment Bill, it was proposed to make the exemption £150, vanishing at £300. To this there was strong opposition and a compromise was reached so that in the Assessment Act (No. 2) 1940 it stands at £200, vanishing at £400.

It has to be remembered that in most of the States there are taxes on income in addition to the regular State income tax, called by various names (wages tax, unemployment relief tax, etc.), and that under these there is a considerable weekly levy on wages, as well as a considerable tax on low incomes which escape the ordinary State income tax of these States with their fairly liberal statutory exemptions. Where these taxes do not operate, the State income tax exemption is low, down to £100 for a person without dependants, and the revenue required for these special purposes is obtained from income tax. This explains the opposition to the original proposal to reduce the Federal statutory exemption to £150, vanishing at £300.

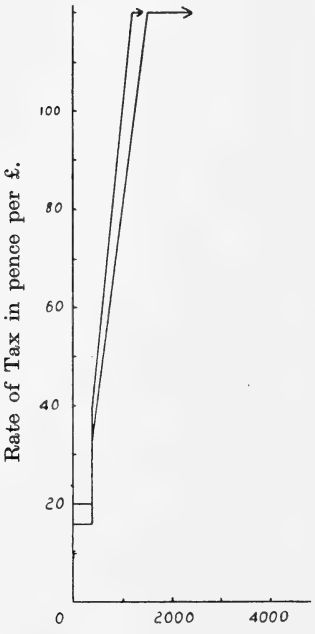


Fig. 10.

In addition to bringing a large number of wage earners and persons with low incomes into the income tax-paying class, the Treasurer had to raise the rates. In the Income Tax Act (No. 2) 1940, with the notation of this paper, they can be expressed as follows:

Earned Income.

When $0 < x \leqslant 400$, $R = 16$.

,, $400 < x \leqslant 1{,}500$, $R = \frac{x}{25}$.

,, $1{,}500 < x$, on the first £1,500, $R = 60$, and on the excess over £1,500 the rate of tax per £ is 120 pence.

Property Income.

When $0 < x \leqslant 400$, $R = 20$.

When $400 < x \leqslant 1{,}200$, $R = \frac{x}{20}$.

,, $1{,}200 < x$, on the first £1,200, $R = 60$, and on the excess over £1,200 the rate of tax per £ is 120 pence.

11. These scales are represented in Fig. 10. Each £ of earned income up to and including the 400th £ pays 16 pence. The 401st £ pays 32·04 pence, a jump up of 16 pence. Then the amounts paid by each successive £ form an arithmetical progression with common difference 2/25ths of a penny up to the 1,500th £, which pays (120 − 0·04) pence. Every £ of the excess over £1,500 pays 60 pence.

Again for property income, each £ up to and including the 400th pays 20 pence. The 401st £ pays 40·05 pence, a jump up of 20 pence. Then the amounts paid by each successive £ form an arithmetical progression with common difference 1/10th of a penny up to the 1,200th £, which pays (120 − 0·05) pence. Every £ of the excess pays 120 pence.

It was to be expected that under the new scales the 1st £ of taxable income would pay more than under the No. 1 Act. It was natural too that the increments in the ascending progressions should be larger than before. But it might have been expected that the range over which the progressions holds would, as in all the earlier Acts, be a large one, so that on the high incomes a much greater part of each £ high up in the range would be taken than of a £ not so far up. Yet for earned income there is a flat rate on the excess over £1,500, while for property income the flat rate holds on the excess over £1,200. Surely with so early an application of a flat rate the principle of ability to pay is forgotten.

The Federal Treasurer told the House[9] that "he had pushed taxation of higher incomes to the limit". This may be true of incomes over £8,000 in Queensland, where on the excess over £8,000 the State taxes on income take about 8s. 5d. from each £, so that on such excess the combined Federal and State taxes on income take about 18s. 5d. from each £. But it does not hold for high incomes in lower-taxed States, and it seems to me that the incidence of the rates of tax in the present Federal Act places a very heavy burden on the middle incomes and a relatively heavy burden on the low incomes, but that high incomes, and in particular very high incomes, in some States carry a burden more easily borne.

It is true that the Income Tax Act (No. 2) 1940 had to be treated as an urgent measure and passed through Parliament quickly. This fact and the obscurity of the schedules defining the rates, as well as ignorance of the principle behind the progressive rate, may explain why discussion was confined mostly to the statutory exemption. That some arrangement must be made with the States, so that the Federal taxation authorities will be able to devise a fairer scale before the next income tax measures are considered, is now generally accepted, and the Federal Government has begun discussions with the Governments of the States with this end in view.

Progressive Rates for Income Tax in the States.

12. For its income tax Tasmania since 1924 has used the original Federal rates, altered from time to time by certain percentages. It is possible that it finds that the ready reckoner issued in 1915 by the Federal authorities saves a good deal of trouble. In all the other States the formulæ depend on a rate R of the type $(ax+b)$. In New South Wales and Western Australia there is but one progression, followed by a flat rate on the excess over a certain sum. The same holds of the scale for earned income in Queensland. In Victoria and South Australia for both kinds of income, and in Queensland for property income, there are either two or three progressions, followed by a flat rate on the excess, when the last of the progressions ends. Suppose that the first ends at x_0 and the second goes from x_0 to x_1. In the first, let $R=ax+b$, and in the second $R=a'x+b'$, with ax_0+b equal to $a'x_0+b'$. We have seen in §5 that there must then be a jump of $(a-a')x_0-(a+a')$ at x_0 in the amount paid by the x_0th £ as compared to that paid by the (x_0+1)th £. Serious discontinuities are introduced in this way in the progressions in these States. In Queensland the position is made still worse by an "Additional Tax" which over certain ranges increases the amount of the earlier tax by certain percentages, varying from 15% to 27½%. Further, there is an extraordinary break with the principle of the progressive tax in the scales for all the States, except Tasmania, when the flat rate is introduced at the end of the last progression. Instead of determining this flat rate by the amount paid by the last £ of the progression, or as

[9] Commonwealth of Australia, Parliamentary Debates, 16th Parliament, 1st Session, p. 88 (1940).

near that as may be, it is in all of them much lower. That this affects the tax on many high incomes is obvious. No such mistake has ever been made in the Federal rates.

Space will permit only a short reference to the scales in force for the financial year 1940-41, and we omit the provisions made for higher taxes on non-residents.

13. New South Wales.

The statutory exemption is £250, diminishing by £1 for every £8 by which the net income exceeds £250 and thus vanishing at £2,250. Discrimination between earned income and property income is made by reducing the taxable earned income by one-fifth, with a maximum reduction of £900, the rate payable on the remainder being that for property.

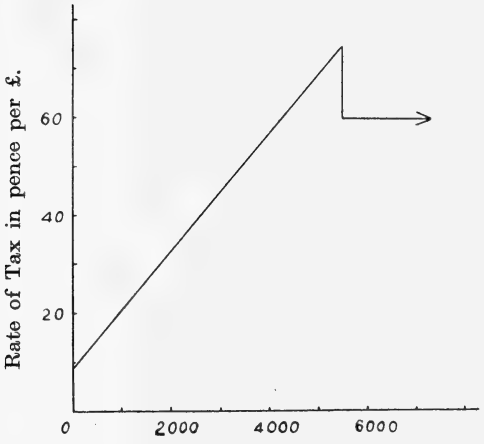


Fig. 11.

When the taxable income is partly earned and partly from property, the earned income is reduced as above, and the remainder plus the taxable income from property is charged at the rate set out for property. This system has been in force since 1936.

The basic rate is as follows[10]: When the taxable income (£x) does not exceed £5,500, $R=9+\frac{3x}{500}$.

When it exceeds £5,500, on the first £5,500, $R=42$ and on the excess over £5,500 the rate of tax per £ is 60 pence.

In Fig. 11 there is a representation of this tax, and it will be seen that the flat rate on the excess over £5,500 should be 75 pence per £, instead of 60 as in the schedule.

The 1st £ pays (9+3/500) pence; each successive £ up to the 5,500th £ pays 3/250ths of a penny more than the preceding; the 5,500th pays (75−3/500) pence.

14. Victoria.

The statutory exemption is £200, vanishing at £600. There are separate formulæ for the rates on earned and property income.

Earned Income.

The scale may be expressed as follows:

When $0<x\leqslant 2{,}500$, $R=7\frac{1}{4}+\frac{3x}{1{,}000}$ ..... (i)

,, $2{,}500<x\leqslant 5{,}000$, $R=10\frac{3}{4}+\frac{x}{625}$ ..... (ii)

,, $5{,}000<x\leqslant 10{,}000$, $R=15\frac{3}{4}+\frac{3x}{5{,}000}$ ..... (iii)

,, $10{,}000<x$, $R=21\frac{3}{4}$ ..... (iv)

[10] At present reduced by 8%, and there is a super tax of 1/− in the £ on so much of the income as exceeds £2,000.

It will be seen that the values of R given by (i) and (ii) at $x=2,500$ are the same, and that the same holds for (ii) and (iii) at $x=5,000$ and (iii) and (iv) at $x=10,000$. There are jumps at these points in the amounts paid by the adjacent £'s, as will be seen from Fig. 12, which gives a representation of this tax.

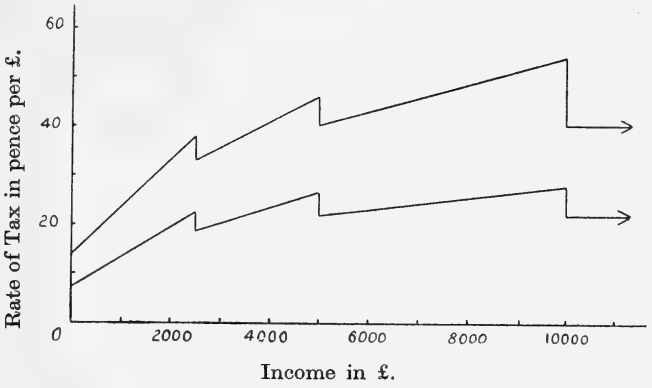


Fig. 12.

It will be noticed that there is a flat rate on the excess over £10,000, and that this has been determined by the value of R given by (iii) for $x=10,000$. It should have been $27\frac{3}{4}$, determined by the amount the 10,000th £ pays, namely $(27\frac{3}{4}-3/5,000)$ pence.

Property Income.

The scale may be expressed as follows:

When $0<x\leqslant 2,500$, $R=14+\frac{3x}{625}$ ..... (i)

,, $2,500<x\leqslant 5,000$, $R=19+\frac{7x}{2,500}$ ..... (ii)

,, $5,000<x\leqslant 10,000$, $R=26+\frac{7x}{5,000}$ ..... (iii)

,, $10,000<x$, $R=40$ ..... (iv)

It will be seen that there are jumps at 2,500, 5,000 and 10,000, as in the other scale, and that the flat rate on the excess over £10,000 should have been 54 pence per £ instead of 40.

This tax is also represented in Fig. 12.

15. Queensland.

The statutory exemption is £150, vanishing at £850. There are separate formulæ for earned and property income.

Earned Income.

The scale may be expressed as follows:

When $0<x\leqslant 8,000$, $R=6+\frac{6x}{1,000}$.

,, $8,000<x$, on the first £8,000, $R=54$,

and on the excess over £8,000 the rate per £ is 60 pence.

Property Income.

The scale may be expressed as follows:

When $0 < x \leqslant 3{,}000$, $R = 12 + \frac{4x}{1{,}000}$.

„ $3{,}000 < x \leqslant 8{,}000$, $R = 6 + \frac{6x}{1{,}000}$.

„ $8{,}000 < x$, on the first £8,000, $R = 54$,

and on the excess over £8,000 the rate per £ is 60 pence.

Both these taxes are represented in Fig. 13.

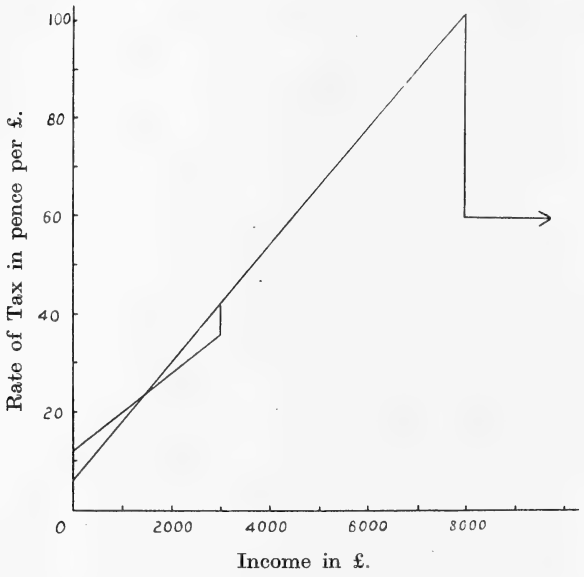


Fig. 13.

In property income there is a jump up of 6 pence at the 3,000th £, and both in earned and property income the flat rate on the excess over £8,000 should be 102 pence per £, instead of 60.

There is also now a Super Tax of 20% of the amount of the tax as given by the above formulæ, with some relief for incomes below £850.

Further, there is an Additional Tax which introduces very large breaks in the continuity of the progression, so carefully arranged by choosing R of the form $(ax+b)$.

When $780 \leqslant x < 850$, 15% is to be added to the amount of the above income tax and super tax.

When $850 \leqslant x < 900$, 16%; when $900 \leqslant x < 950$, 18%; when $950 \leqslant x < 1{,}000$, 20%; and when $1{,}000 \leqslant x$, $27\frac{1}{2}$%.

There is not much use in providing a scale with each £ paying 0·012 or 0·008 pence more than the preceding £ if these steps are taken at intermediate points. The progressive principle can quite easily be adhered to and the higher incomes made to pay at desired rates, but a new formula allowing for the super tax and additional tax would have to be devised.

16. South Australia.

The statutory exemption is £100, vanishing at £1,000. There are separate formulæ for earned and property income.

The scales can be expressed as follows:

Earned Income.

When $0 < x \leqslant 1{,}000$, $R = 17 + \frac{2x}{1{,}000}$.

„ $1{,}000 < x \leqslant 7{,}000$, $R = 13 + \frac{6x}{1{,}000}$.

„ $7{,}000 < x$, $R = 55$.

Property Income.

When $0 < x \leqslant 1{,}000$, $R = 26 + \frac{2x}{1{,}000}$.

,, $1{,}000 < x \leqslant 7{,}000$, $R = 22 + \frac{6x}{1{,}000}$.

,, $7{,}000 < x$, $R = 64$.

These taxes are represented in Fig. 14. In both scales there is a jump up of about 4 pence at £1,000. In earned income the flat rate on the excess should be 97 pence per £, instead of 55, and in property income 106 pence per £ instead of 64.

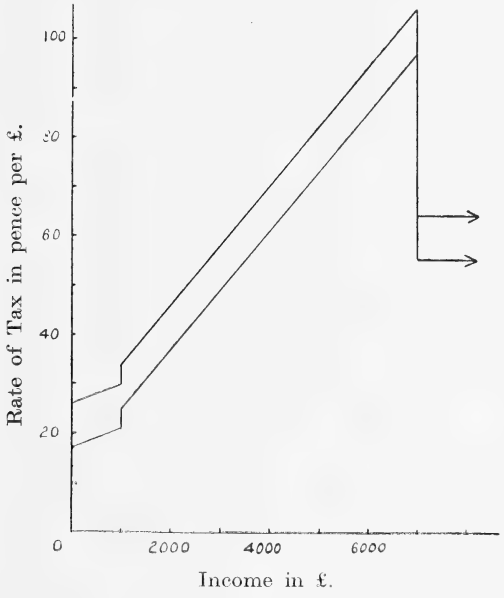


Fig. 14.

17. **Western Australia.**

In 1918 this State introduced a continuous progressive tax "at the rate of twopence in respect to every pound sterling of taxable income chargeable plus an additional rate thereon of 0·006 of a penny for every pound sterling by which the income chargeable from all sources exceeds £100. Provided that the rate in the pound shall not exceed two shillings and sixpence."

The above statement, in the notation of this paper, can be put as follows:

When $0 < x \leqslant 100$, $R = 2$.

$100 < x \leqslant 4{,}766$, $R = 2 + \frac{6(x-100)}{1{,}000}$.

$4{,}766 < x$, $R = 30$.

With some modifications, including the raising of the maximum rate to four shillings, reached at £6,672, this scheme has been in force till the present financial year, when a new scale has been adopted. The other taxes on income (hospital tax, financial emergency tax) have been dropped, and the revenue previously obtained from them is to be provided by the revised income tax.

There is, as before, no distinction between earned and property income. The statutory exemption for a single person without dependants is £100 less

£2 for every £1 by which the income exceeds £100 ; for a person with dependants, £200 less £2 for every £1 by which the income exceeds £200.

The scale is as follows :

When $0 < x \leqslant 4{,}500$, $R = 9 + \frac{x}{100}$ ..... (i)

$4{,}500 < x$, $R = 54$ ..... (ii)

This tax is represented in Fig. 15.

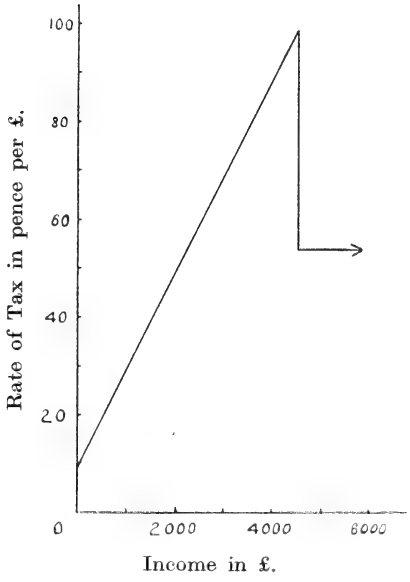
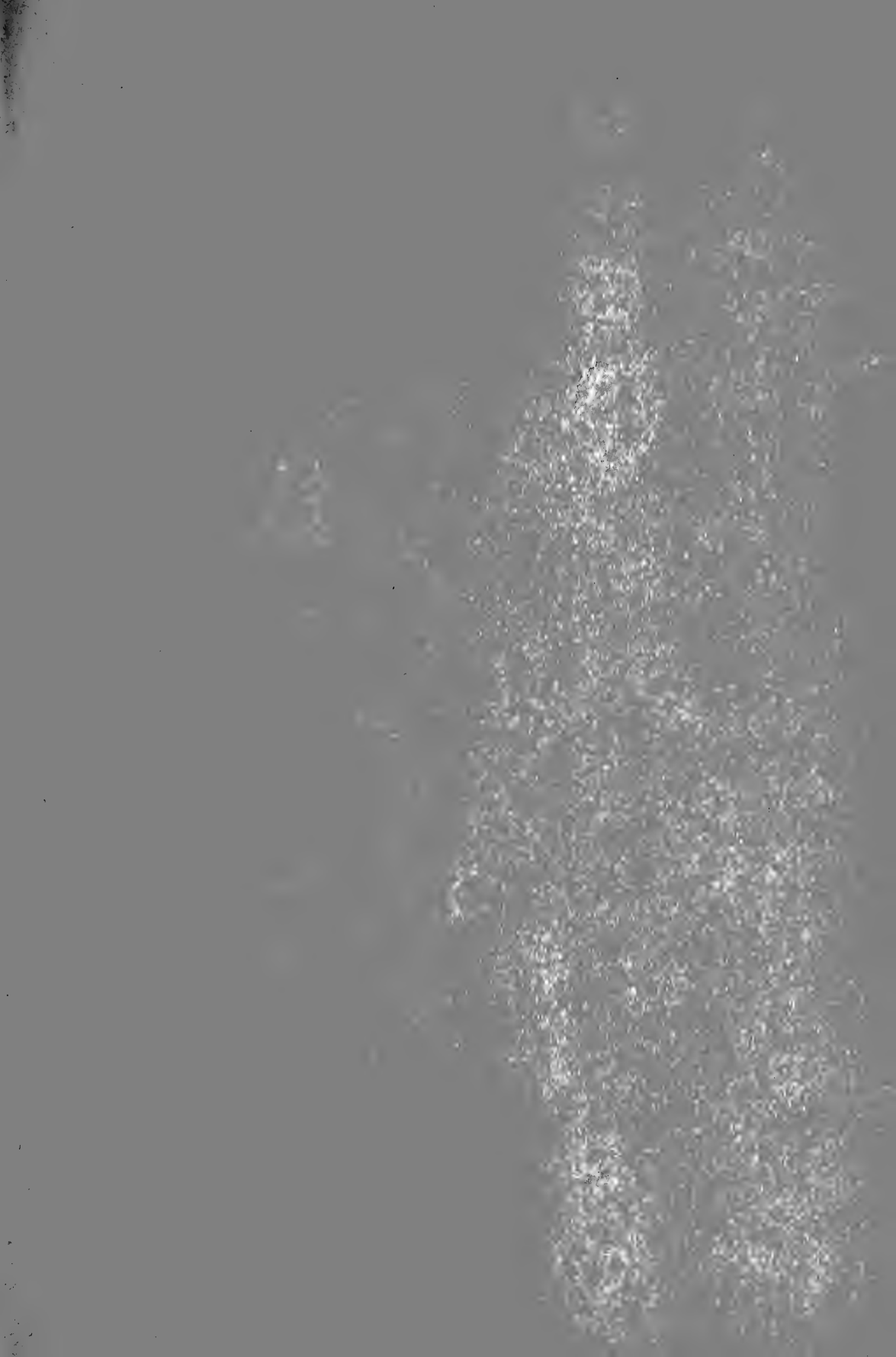


Fig. 15.

It will be seen that (i) and (ii) give the same value at $x = 4{,}500$, but that the flat rate on the excess over £4,500 is much lower than the figure indicated by the amount the 4,500th £ pays. Instead of 54 pence per £, it should be 99 pence.



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CONTENTS

VOLUME LXXV

Part II

Page.

ART. V.—Clarke Memorial Lecture. The Climate of Australia in Past Ages. By C. A. Sussmilch, F.G.S. (Issued September 11, 1941) 47

ART. VI.—An Examination of the Essential Oils Distilled from the Tips and Normal Cut of *Eucalyptus polybractea*. By Philip A. Berry, M.Sc., and Thomas B. Swanson, M.Sc. (Issued September 11, 1941) 65

ART. VII.—The Jurassic Fishes of New South Wales. By R. T. Wade, M.A., Ph.D. (Issued September 11, 1941) 71

ART. VIII.—Remarks on Goodness of Fit of Hypotheses and on Pearson's χ Test. By D. T. Sawkins, M.A. (Issued September 11, 1941) 85

THE CLIMATE OF AUSTRALIA IN PAST AGES.*

By C. A. Sussmilch, F.G.S.

Introduction.

I desire, first of all, to thank the council of the Royal Society of New South Wales for the honour conferred in asking me to deliver the Clarke Memorial Lecture for this year; I do consider it a great honour to be associated in this way with the memory of the late Rev. W. B. Clarke. This eminent scientist, the pioneer of the geologists of this State, laboured for many years, practically single-handed, in what was, at that time, a thinly populated region of vast extent, with only very primitive means of transport; under these very adverse conditions he established the succession of the sedimentary formations of New South Wales. Upon the foundations so ably laid by him the superstructure of our present knowledge of its geological history has been built. It is surprising how well these foundations have stood the test of time, and they stand today as an enduring record of his great ability and of the patient care with which he applied himself to his work. It is to the accumulated geological knowledge erected upon these foundations by subsequent geological workers that we turn to look for evidence of the past climates of Australia.

The climate which prevails in Australia today is based primarily upon its position with respect to the equator; those parts (about one-third) which extend northwards of the Tropic of Capricorn, lie within the tropics and enjoy a typical tropical climate; the rest of the continent lies within the temperate zone and enjoys a relatively mild climate, no part of it, not even Tasmania, projecting sufficiently far south of the equator to have a really rigorous climate. Other factors such as altitude, ocean currents, prevailing winds, proximity or otherwise to the shoreline, all exercise some control over the existing climate, but only to a minor degree, except with regard to rainfall, over which they have considerable influence; not much of Australia is sufficiently elevated to be influenced to any great extent by that factor.

As will be shown presently, the climate of Australia has shown very great variations in the past as compared with what it is today; there have been very long periods of time when much colder conditions were in existence, and again even longer periods during which the climate was notably warmer than an present. Human history goes back only some 150 years in this continent and does not record anything more than very minor changes of climate, apart from variations in rainfall, during that time. In the Northern Hemisphere human history goes back for about 8,000 years, and even in that much longer period only minor changes have been recorded, and these appear to have occurred in cycles. In view of this statement the layman may well ask how it is possible to learn of changes of the world's climate in prehistoric times; the answer to this question is to study the rocks which we see everywhere around us; each rock is a book, one of nature's own books, and each one of these books has a story to tell, if we but know how to read it. Many rocks both in their composition and in their

* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, May 22, 1941.

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GEOLOGIC TIME CHART

INDICATING CLIMATIC VARIATIONS

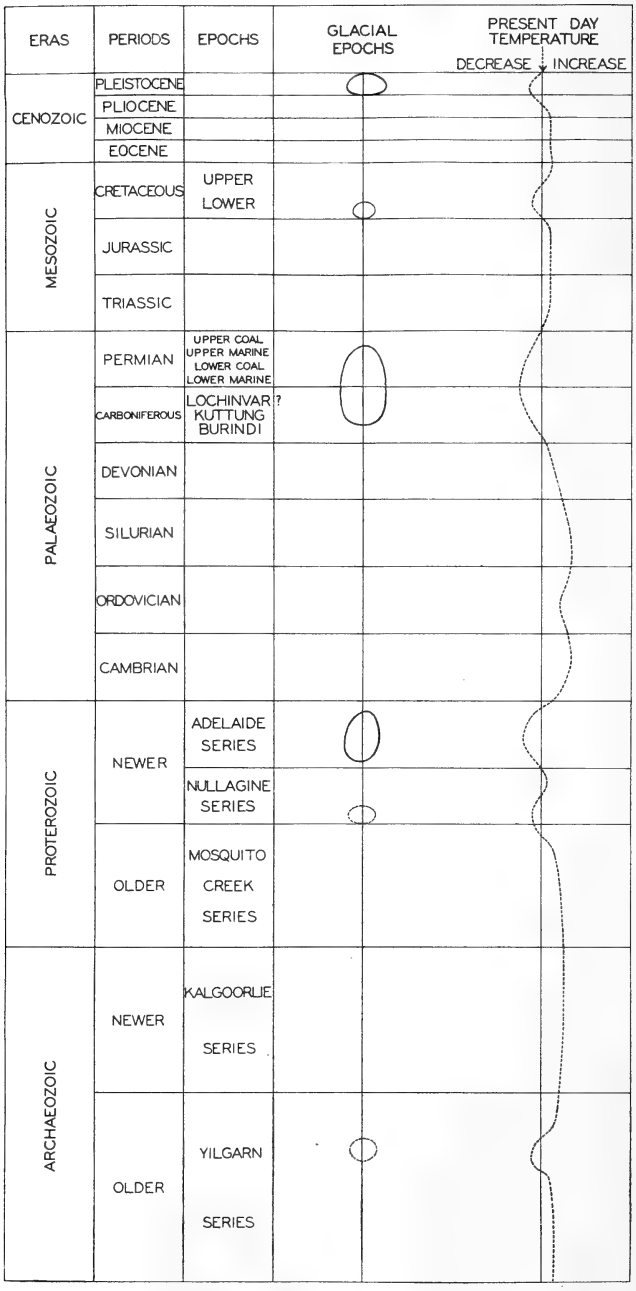

Fig. 1.

structures give evidence of the climatic conditions under which they were formed; many sedimentary rocks also contain the fossilised remains of once living animals and plants, and some of these afford evidence of the climatic conditions existing at the time they were alive. It is not necessary to describe here all of these evidences in detail; such description can be found in all geological text books, but they will be referred to later briefly when necessary.

In my discourse it will be necessary to refer to the various subdivisions of geological time; these are given in Text-figure 1.

From the above table it will be seen that there are five primary subdivisions called eras, and that each of these is divided into a varying number of subdivisions called periods, and that these latter are further divided into epochs. The classification given is not a complete one, but is sufficient for our present purpose. The actual length of time in years represented in this chart will vary from 100 to 1,800 millions of years, according to the factors used in computing it; the longer period is probably nearest to the truth. It is usual in discussing past variations of climate to refer them to our existing climate as being a normal one, and to look upon the colder and warmer periods of the past as being abnormal, but this is not necessarily correct, as some geologists consider our present climate to be abnormal, and the world to be still in one of the inter-glacial epochs of the last great Ice-age.

In discussing the probable climates of the various geological periods it will be assumed that Australia as a continent has always occupied its present position with regard to the equator, but this also is not necessarily correct, because there is one school of geologists which considers that all of the continents have in the past changed their relative positions from time to time, and are in fact still doing so. If this view were correct it is obvious that, if in one of the past geological periods Australia had occupied a position far to the south of that now occupied, it would have had a climate much colder than that of today without any necessary alteration in the climate of the world as a whole. This belief in drifting continents is not, however, held by all geologists, and we will assume for our present purpose that the position of Australia as a whole has remained constant throughout geological time.

The Archæozoic Era.

Rocks of this age occur over very wide areas in Australia, particularly in Western Australia, South Australia, and the Northern Territory; they are, however, so much metamorphosed and altered that such of their original characters as might have given evidence of the climatic conditions under which they were laid down have been largely obliterated. These conditions are not peculiar to Australia, but exist also in all other parts of the world where strata of this age occur. There does occur, however, on the Kanowna Goldfield of Western Australia, a series of conglomerates belonging to the Yilgarn series which are not much altered, and T. W. E. David has given it as his opinion that they may have had a flurio-glacial origin and show evidence, therefore, of a cold climate at the time they were being deposited. This view has, however, not been accepted by Western Australian geologists. Such evidence is not limited to Australia; there occurs in central Canada a similar series of conglomerates apparently of similar age, which A. P. Coleman[1] definitely considers to have had a glacial origin and which he has called the Timiskamian or Sudbury Boulder conglomerates, and with these there has been found in many localities beds of varve-like shales showing seasonal banding. In India also there occur the Darwar conglomerates, considered by Foote to be similar in character and age to those of Canada. There appears to be some evidence, therefore, of a world-

wide refrigeration of the climate during some part of the Archæozoic Era, in which Australia may have participated.

The Proterozoic Era.

Rocks of the Proterozoic age are very widespread in Australia, particularly so in Western, Central, and South Australia. The Proterozoic formations of Western Australia have been divided into an older division called the Mosquito Creek Series, and a newer division called the Nullagine Series. The older series consists mainly of schists, phyllites and jaspers, with some thick beds of dolomitic limestone, and the presence of the limestone beds and the fact that some of them are dolomitised suggests that at the time of their deposition the climate was warm to hot, but in the absence of recognisable fossils this evidence is not altogether conclusive.

The Nullagine Series outcrops extensively in the Pilbarra District, and here they have at their base a series of coarse conglomerates ranging up to 500 feet in thickness ; no definitely glacially striated boulders have yet been obtained from these beds, but T. W. E. David[2] considered that they may have had a fluvio-glacial origin. Above these conglomerates thick beds of limestone occur, but they have not yet yielded any fossils. In Central Australia the Nullagine Series contains many very thick beds of limestone, some of which contain an abundance of fossil marine plants (Algæ) which have been referred to the Cryptozoa ; these algal limestones extend over very wide areas, and it has been suggested that they indicate at least a mild, if not a warm, climate at the time of their deposition.

In South Australia the Upper Proterozoic strata are known as the Adelaide Series and they have been fully described by W. Howchin[4] ; he has subdivided them as follows (in descending order) :

11. The Brighton limestone.
10. Banded siliceous limestones.
9. Tapley's Hill ribbon slates with occasional pebbles of quartzite.
8. Impure dolomitic limestones.
7. The Sturtian Tillite.
6. Quartzites and claystones.
5. The Blue Metal limestones.
4. The Upper Phyllites.
3. The Torrens Limestone.
2. Phyllites, slates and shales.
1. The Basal Beds (conglomerates, grits and sandstones).

These beds have an aggregate thickness of about 13,000 feet. The most interesting feature of this section is the Sturtian Tillite, which ranges up to 1,500 feet in thickness ; it is a typical glacial till containing numerous glacial erratics ranging individually up to 10 feet in diameter, and striated and facetted pebbles are common. Some thin lenticular beds of a gritty limestone occur interstratified in the Tillite. Howchin originally considered these beds to be of Cambrian age, but they are now generally accepted as being of Upper Proterozoic age.

Howchin considers that the Sturtian Tillites were laid down on the sea floor by floating ice, but that the snow-fields were not very far distant, as many of the erratics appear to be identical with certain older rocks outcropping immediately to the south and west of the glacial beds. He has traced these glacial beds northwards to Hergott in Lat. 29° 40″ South.

From this northern area D. Mawson has,[5] in the foothills of the Flinders Range, measured the following section :

	Thickness.
13. Glacial Series—tillites, conglomerates and quartzites	800 feet +
12. Calcareous Series—algal limestone with some sandstone and shale	3,200 ,,
11. Arenaceous and Argillaceous beds	2,700 ,,
10. Dolomitic marble	1,000 ,,
9. Chocolate shales	350 ,,
8. Limestones, including algal, dolomitic, and oolitic varieties, with some shale bands	450 ,,
7. Oolitic limestones	560 ,,
6. Limestones with shaly and clayey layers	950 ,,
5. Dolomitic limestone	130 ,,
4. Algal limestones	120 ,,
3. Calcareous shales and limestones	500 ,,
2. Laminated shales	750 ,,
1. Glacial and fluvio-glacial beds	1,000 ,,
Total	12,510 ,,

Mawson calls this series of strata the Munyallina Beds and correlates them with the Adelaide Series from near Adelaide already referred to. In describing the lower glacial horizon Mawson states : " At the base of the section is a glacial and fluvio-glacial formation which includes true tillites ; near the base the boulders are dominantly basic lavas derived from the underlying formation, and also large blocks of dolomitic limestone also from the underlying formation ; a couple of hundred feet above the base the boulders include quartzite, granite and quartz-porphyry ranging up to 3′ 6″ in diameter, and pebbles have been found exhibiting glacial striæ ". Mawson states further, " some of the beds are obviously glacially transported and accumulated and that it is quite obvious that, during the time the beds were being deposited, land ice existed in this region and as the glacial beds are followed immediately and conformably by an undoubted series of marine strata, the land over which the ice travelled was not much above sea-level ; a glacial climate is therefore indicated ". This lower glacial horizon is separated from the upper one by a thickness of over 10,000 feet of strata, mainly limestones, and many of these contain marine algæ such as *Girvanella*, *Collenia* and *Mawsonella*. Mawson considers that these algal limestones are indicative of a warm climate and comes to the conclusion that " the climatic record is a remarkable one varying from severe glacial to probably warm arid conditions and again glacial within the period of deposition of these beds ". Mawson correlates the topmost glacial bed with the Sturtian Tillite of the Adelaide Series, and, if this is so, possibly the lowest glacial bed may be the equivalent of the conglomerates (possibly fluvio-glacial) which occur at the base of the Nullagine Series of Western Australia. W. G. Woolnough[7] has also described some of the Proterozoic strata of the Flinders Range and has recorded evidence of aridity of climate in the red colour of some of the sedimentary rocks, the presence of sun-cracks, and in certain other features.

The glacial beds of the Adelaide Series are known to outcrop over an area 450 miles long in a north-south direction and 200 miles long in an east-west direction, where they extend into the Broken Hill district of New South Wales, and over this large area not only are the tillites very thick but the glaciers or ice-sheets must have extended down to sea-level, and as already pointed out

extended northwards to Lat. 29° 40′ South, one must conclude therefore that the climate of Australia in the Upper Proterozoic was very cold and remained so for a considerable time.

It is interesting to note that this refrigeration of the climate was not limited to Australia, because glacial beds of similar age, the Numee Tillites, occur in South Africa, extending there also to Lat. 29° S.; and glacial beds have also been found from such widely separated localities as Utah, U.S.A., Simla in India, and the Yangtse Cañon in China (the latter may be of Lower Cambrian age). This widespread occurrence of glacial beds in both Northern and Southern hemispheres indicates a worldwide refrigeration of the climate in Upper Proterozoic times, a refrigeration even more pronounced than that of the recent Pleistocene Ice age, when land ice only reached as near the equator as Lat. 38° as against Lat. 29° of the earlier era.

The Cambrian Period.

Marine strata of Cambrian age occur in South Australia immediately overlying the Adelaide Series described in the last section, and these strata extend as a broad belt northwards through Central Australia and western Queensland and thence into the Northern Territory. These Cambrian strata contain an abundance of the fossils of once-living marine animals including trilobites, brachiopods, pteropods and gasteropods, but the most important of the fossils belong to an extinct group of organisms called the Archæocyathinæ. These animals in their skeletal structures, which are calcareous, have some resemblance to both sponges and corals, and like the latter they built extensive reefs much like existing coral reefs. The Archæocyathinæ had become extinct by the close of the Cambrian period, and we have therefore no direct knowledge as to the climatic conditions under which they lived, but from their close resemblance to the reef-building corals it is considered that, like them, they lived in warm tropical seas, and if this assumption is correct, Australia down to its southern margin must have had a warm tropical climate in Cambrian times; the other fossils found in the Cambrian rocks do not oppose this view. This extinct group of organisms has also been found as fossils in the Antarctic continent as well as at various localities in the Northern Hemisphere, and this suggests that not only Australia, but practically the whole world had a much warmer climate in Cambrian times than it has today.

In some parts of South Australia the topmost beds of the Cambrian System consist of cross-bedded red sandstones interstratified with chocolate-coloured shales and some thin beds of limestone; W. Howchin[4] has suggested that there is a strong probability that these strata accumulated under arid or even semi-desert conditions for the following reasons: (*a*) the prevailing red colour of the rocks; (*b*) many of the limestones are oolitic or nodular with wavy and concentric structures that appear identical with surface travertine that is forming today in the drier parts of Australia; (*c*) the newest members consist of red, friable, cross-bedded sandstone closely resembling wind-blown sand dunes. These conclusions, of course, would apply only to the limited area in which these strata now occur.

The Ordovician Period.

The evidence of climatic conditions of this period in Australia are not very definite. Strata of this age are widespread, particularly in Victoria, New South Wales, and Central Australia. In the first two States the strata consist mainly of marine shales and sandstones, and the contained fossils consist almost entirely of graptolites, an extinct group of hydrozoa. These animals inhabited the surface waters of the ocean, and we find them preserved in abundance in

Ordovician strata all over the world ; they therefore had a very wide geographical range. The group became extinct in the next geological period (Silurian), and they afford therefore no direct information as to the climatic conditions under which they lived. The Ordovician strata of Central Australia do not contain fossil graptolites, but have yielded an abundance of other marine fossils such as brachiopods, mollusca and trilobites ; these also are not very definite climatic indicators. There is, so far as we know, an entire absence of reef-building corals in Australia, although they were living in other parts of the world, and their absence, together with the extinction of the Archæocyathinæ, might possibly suggest cooler conditions. In the Northern Hemisphere, on the other hand, limestones of Ordovician age containing fossil reef-building corals are abundant, and, as these extend as far north as Baffin Island, they indicate a tropical climate extending well into the Arctic region at that time. It seems probable, therefore, that the climate of Australia in Ordovician times was still warm, although perhaps not quite so warm as it had been in Cambrian times.

The Silurian Period.

For this period the rocks yield quite definite evidence as to the nature of the climate, as we find an abundance of limestones of Silurian age crowded with the remains of once-living reef-building corals ; such coralline limestones occur in a broad belt of strata extending from Tasmania northwards through Victoria, and New South Wales to the Chillagoe district of north Queensland ; and it would appear that what was then the eastern coast of Australia was as that time fringed with coral reefs along its whole length. As reef-building corals

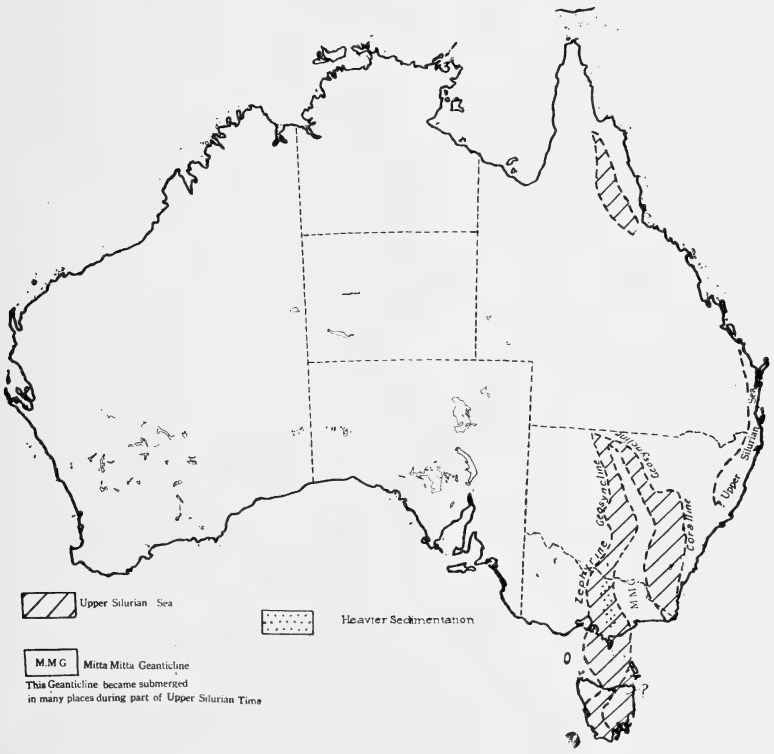

Fig. 2.—Areas in Australia in which fossil corals of Silurian age occur.
(Compiled by E. C. Andrews.)

are abundant in our present day seas, we know something about the conditions necessary for them to flourish. These conditions include the following : (*a*) the temperature of the sea-water must not fall below 68° F. ; (*b*) the water must not exceed 240 feet in depth ; (*c*) the sea-water must be in general free from the presence of much mechanical sediment such as mud and sand. All of these conditions exist along the coast of Queensland today and we find a continuous belt of coral reefs extending from Cape Yorke southwards nearly to the latitude of Brisbane. South of this point no coral reefs exist for the one and only reason that the temperature of the sea-water there is too low for their requirements. The fact that coral reefs in Silurian times flourished in Tasmania, some 1,200 miles south of their present habitat, indicates a considerably warmer climate than that of today.

The Northern Hemisphere affords even more striking evidence, as coralline limestones of this age exist well into the Arctic regions. We can say, therefore, without hesitation, that the climate of Australia was definitely tropical during the Silurian period, just as it was in other parts of the world.

The Devonian Period.

The warm conditions of the Silurian period continued into the succeeding Devonian period, because we find coralline limestone of Middle Devonian age occurring so far south as Victoria (the Buchan and Bindi Limestones). The sea disappeared from Victoria at the end of Middle Devonian times, but in New South Wales there was in the Upper Devonian a very extensive transgression of the sea which extended from the present south coast north-westwards into the Cobar district ; this was a shallow sea and in it were deposited coarse sediments for the most part such as sandstone and conglomerates with some shales ; in some localities the prevailing red colour of the beds and other factors suggest semi-arid conditions of climate. This Upper Devonian sea was inhabited by an abundance of marine life, principally brachiopods and pelecypods, and there were also numerous marine fish. The presence of an abundance of the fossil stems of land plants in some of these marine beds indicates that the land in places supported an abundant vegetation, so that the climate could not have been semi-arid everywhere. The absence of reef-building corals in these Upper Devonian strata suggests that the climate may have become somewhat less tropical than it appears to have been earlier in the period.

The Carboniferous and Permian Periods.

As the climatic conditions of these two periods appear to have been very similar, it will be convenient to consider them together. A study of the strata deposited during this part of Australia's history gives evidence of some very remarkable climatic changes. At the beginning of the Carboniferous period the climate was still warm, somewhat warmer than it is today, but conditions very soon became colder ; by the middle of the period a refrigeration of the climate had taken place of such magnitude that much of the southern half of Australia was covered by great glaciers and ice-sheets, which in places extended down to sea-level. From then on until the middle of the Permian period there was a succession of glacial epochs separated from one another by relatively warmer interglacial epochs. The climate then began to warm up again, glacial conditions disappeared during the upper part of the Upper Marine epoch, and during the Upper Permian (Upper Coal Measure epochs) the climate was again warm enough to support extensive forests of large trees ; the evidence for these climatic changes is as follows.

At the beginning of the Carboniferous period an extensive epicontinental sea covered a large part of eastern Australia, extending from the Hunter River district in New South Wales northwards to the Cairns district in Queensland, a

distance of upwards of 1,000 miles; it extended from 50 to 150 miles inland from the present-day shoreline. The region covered by this sea was undergoing intermittent subsidence throughout the whole of the Carboniferous and Permian periods, and on it was deposited a great series of sedimentary strata aggregating many thousands of feet in thickness; some were deposited under marine conditions, some in fresh-water lakes and some on actual land surfaces. The strata so deposited have been intensively studied in the Hunter River district of New South Wales and here they have been subdivided as shown in Table 1.

(*a*) *The Burindi Series.* This is a marine series including some beds of limestone, and in the lower part of the series these contain fossil reef-building corals, some of which are found as far south as Taree in New South Wales, that is several hundreds of miles to the south of the present-day limit of these organisms. We must conclude, therefore, that in early Burindi time the climate was still warm, although perhaps not as warm as it had been in the preceding Silurian and Devonian periods. The reef-building corals, however, soon disappeared in New South Wales, and, although marine fossils are abundant in the upper parts of the Burindi Series, the individuals are all small and the fauna as a whole may be described as a pauperitic fauna; the indications are, therefore, that the climate in the upper part of Burindi time was becoming cooler.

(*b*) *The Kuttung Series.* In New South Wales an uplift of the land now took place which caused the Carboniferous sea to retreat northwards, and on the land surface so produced was deposited one of the most remarkable series of strata found in Australia. There was first deposited a remarkable thickness of conglomerates (the Wollarobba Conglomerates), ranging up to 2,000 feet in thickness; these do not appear to have had a glacial origin, in most localities in which they occur, but from the Gosforth district some striated pebbles have been obtained; immediately above them some glacial varve-shales occur; this constitutes the first glacial horizon shown in the table. This was followed by a great series of volcanic rocks, lavas and tuffs, ranging up to 2,500 feet in thickness, with which are interstratified many beds of conglomerate with boulders two feet or more in diameter. Then follows a formation called the Main Glacial Beds (No. 2 glacial), ranging up to 6,000 feet in thickness. In this series there are definite glacial deposits such as tillites, fluvio-glacial conglomerates and varved shales; the tillites contain boulders ranging up to 10 feet in diameter and also many striated pebbles, and at one locality they rest upon a striated pavement. The varved shales show contemporaneous contortion in certain of the beds, and some contain occasional large pebbles and in some places regular pockets of pebbles. These typical glacial formations occur on a number of distinct horizons which are separated from one another by various thicknesses of non-glacial beds (shales, sandstones and tuffs), in some of which are found fossil plants (the Rhacopteris flora). These conditions suggest a succession of advances and retreats of the ice-sheets with intervening interglacial epochs. The seasonal banding of the varve shales shows that seasonal variations of temperature took place just as they do today.

Glacial beds with similar fossil plants have been found by J. H. Reid in Queensland in Lat. 17° 30′ South. Some of the terrestrial glacial beds of Victoria and South Australia may be of similar age to the Kuttung glacial beds of New South Wales, but their actual age is uncertain and they have usually been referred to the Lower Permian epoch. There can be no doubt that a very marked refrigeration of the climate took place during Kuttung time.

(*c*) *The Lochinvar Series.* In the Hunter River district the Kuttung Series is followed without any apparent angular unconformity by a series of marine strata (perhaps in part lacustrine) called the Lochinvar Beds. In a paper written by the late T. W. E. David[3] and the writer in 1931 these beds were

TABLE 1.

Subdivisions of the Carboniferous and Permian Systems of the Hunter River District of New South Wales indicating the Glacial Horizons.

				Feet.	
Permian	Upper Permian.	Upper Coal Measures			
	Middle Permian.	Upper Marine Series.	Mulbring Stage	1,500–3,000	
			Muree Stage (with Bolwarra Conglomerate)	400	5th Glacial Horizon B.
			Branxton Stage (with glacial erratics in upper part).	1,500–3,000	5th Glacial Horizon A.
	Lower Permian.	Lower Coal Measures.		230	
		Lower Marine Series. (upper part).	Farley and Rutherford Stages.	1,500–3,000	
			Allandale Conglomerate with glacial erratics.	200	4th Glacial Horizon.
	? Lower Permian or Upper Carboniferous.	Lower Marine Series. (lower part).	Lochinvar Marine Stage.	2,400	
			Lochinvar Glacial Beds.	300	3rd Glacial Horizon.
		(? Unconformity.)			
Carboniferous.	Middle Carboniferous.	Kuttung Series.	Main Glacial Stage (with Rhacopteris Flora).	4,700	2nd Glacial Horizon.
			Volcanic Stage.	2,500	
			Basal Stage (Wollarobba Conglomerates and Tuffs).	2,300	1st Glacial Horizon.
	Lower Carboniferous.	Burindi Series.		+5,000	

placed tentatively in the Upper Carboniferous epoch, which, if correct, would mean that they followed the Kuttung sedimentation without any marked time break ; much geological field work has been done in various parts of Australia since then and many geologists are now of the opinion that these beds are of Lower Permian age, and that there is consequently a very definite time break between the close of the Kuttung epoch and the laying down of the Lochinvar Beds ; even if this be so the time break represented, that is the time break between glacial horizons 2 and 3, would probably be of no greater magnitude than that which exists between some of the other glacial horizons, say, for example, that between horizons 4 and 5, which are both within the Permian system and which are separated by nearly 4,000 feet of strata, including both marine beds and fresh-water beds (the Lower Coal Measures) ; we may therefore still consider that both the Carboniferous and Permian glacial beds belong to one great climatic epoch.

The Lochinvar Beds begin with a series of glacial beds (3rd glacial horizon) followed by a thickness of 2,400 feet of marine strata, which constitute the lower part of the Lower Marine Series.

(*d*) *The Lower Marine Series.* The lower part of this series has just been referred to as the Lochinvar Beds ; immediately above these are the Allandale conglomerates, containing some glacial erratics (4th glacial horizon), and these in turn are followed by some 1,500 to 2,000 feet of marine strata containing an abundance of marine fossils, but no reef-building corals.

(*e*) *The Lower or Greta Coal Measures.* This is a series of fresh-water strata some 230 feet in thickness containing two important coal seams, one of which reaches a thickness of 30 feet of coal. An abundance of fossil plants (the Glossopteris flora) is associated with these strata. The presence of this fresh-water series with its coal seams and fossil plants between two glacial series (horizons 4 and 5) indicates a marked but temporary warming up of the climate, in other words a typical interglacial epoch.

(*f*) *The Upper Marine Series.* This follows conformably upon the Lower Coal Measures and consists of marine strata ranging up to 6,000 feet in thickness. Two glacial horizons occur in this series ; the lowest of these (horizon 5A) is situated in the upper part of the Branxton Beds, where many large glacial erratics have been found scattered through the marine beds ; these include boulders of limestone containing Silurian corals and boulders of quartzite containing Devonian brachiopods. Such rocks occur *in situ* at the present day in the Blue Mountains on what was the western shoreline of the upper marine sea in Permian times. It is obvious that at this time land ice reached sea-level, broke away as icebergs which melted as they floated across this sea, dropping their load of morainic material on the sea bottom. Some 500 feet above these beds are the Bolwarra Conglomerates (glacial horizon 5B) ; this is a typical marine glacial boulder bed crowded with glacial erratics and is the highest and last of the glacial beds of the Carboniferous-Permian Series. The boulders found in horizon 5A and 5B consist in general or rocks quite different to those found in the Kuttung glacial horizons and must have come in the main from a different source ; they cannot be redistributed material from the Kuttung glacial beds. Those parts of the Upper Marine Series above the Bolwarra Conglomerates show no evidences of glacial conditions, but there is no change in the marine life occurring in them as fossils.

(*g*) *The Upper Coal Measures.* This is a fresh-water series ranging up to 6,000 feet and including many coal seams ; these strata contain an abundance of fossil plants similar for the most part to those found in the Lower Coal Measures. In one locality many small fossil insects have been found. In some beds, particularly just above some of the coal seams, many fossil trees occur ranging

up to eighteen inches in diameter, showing that at times the land was covered with fairly dense forests. All of these facts indicate that glacial conditions had ceased and the climate had become warmer, but not necessarily tropical; R. J. Tillyard, who has described the fossil insects from this series, considered that their small size indicated that the climate was still somewhat rigorous.

Both terrestrial and marine glacial beds of Permian age occur in Tasmania; at Wynyard, on the north coast, the glacial beds are 1,500 feet thick and contain erratics up to five feet in diameter, and they rest upon glacially striated pavements; the striæ have a NNE trend indicating that the ice was moving in that direction. Both the Allandale and the Branxton glacial horizons are represented in Tasmania. Terrestrial glacial beds are also widespread in Victoria and South Australia; in the latter State they range up to 900 feet in thickness and in both States extensive glaciated pavements underlie these beds; there is some uncertainty as to whether these glacial beds of Victoria and South Australia are to be correlated with the Carboniferous or Permian glacial beds of New South Wales, but there is no question that they are of Upper Palæozoic age. In Western Australia marine glacial beds exist over very extensive areas occurring near the base of the Permian formations of that State, and in the Kimberley district they extend northwards to Lat. 18° S. In Queensland, also, marine glacial beds of Permian age extend well into the tropics.

These glacial formations of Carboniferous and Permian age appear to have their greatest development in the south-eastern parts of Australia. In New South Wales there were at least five important glacial epochs as follows:

Glacial Horizon.		*Thickness.*
5B	Bolwarra Conglomerate	40 feet
	Marine strata	500 ,,
5A	Branxton Erratic horizon	10 ,,
	Marine strata	2,000 ,,
	Lower Coal Measures	100-230 ,,
	Marine strata	1,800 ,,
4	Allandale Beds with glacial erratics ..	270 ,,
	Marine strata	2,400 ,,
3	Lochinvar glacial beds	300 ,,
	(?) Unconformity representing part of Upper Carboniferous time.	
2	Main glacial stage of the Kuttung Series ..	4,700 ,,
	Volcanic state of the Kuttung Series ..	2,500 ,,
1	Varved shales	100 ,,
	Wollarobba Conglomerates and tuff with some striated pebbles	2,300 ,,

It will be noted that great thicknesses of strata separate most of these glacial horizons from one another; for example there are over 3,900 feet of strata between horizons 4 and 5 and 2,400 feet of strata between horizons 3 and 4. If an unconformity exists between horizons 2 and 3, a considerable thickness of strata might be missing there. As the thickness of strata between horizons 5A and 5B is only 500 feet, these two might be considered as belonging to one horizon. It would seem, therefore, that during the Carboniferous and Permian periods there were five epochs of heavy glaciation separated from one another by four quite long interglacial epochs. This does not necessarily mean that glacial conditions disappeared entirely from Australia during these interglacial epochs, but that the ice fields must have become much restricted during such periods. In the case of the interglacial period between horizons 4 and 5, with its coal measures and thick coal seams, glacial conditions probably almost ceased at that time.

Besides these major oscillations of climate during this period, the detailed section of the Kuttung Series indicates also minor oscillations ; as has already been shown, there are in the Main Glacial series of the Hunter River district at least four horizons of tillites and varve shales separated from one another by moderate thicknesses of non-glacial strata, indicating successive advances and retreats of the ice-sheets.

Conclusive evidence exists, therefore, that throughout the greater part of the Carboniferous and Permian periods great ice-sheets existed in Australia, and that during the Kuttung epoch land ice existed as far north in Queensland as Lat. 30° S., and that during Permian time drifting ice deposited morainic material as far north as Lat. 18° S., and, as these occurrences extend much nearer to the equator than similar deposits of Pleistocene age, the refrigeration of the climate in Upper Palæozoic time must have been greater than that which occurred in the last great Ice Age, when no land ice appears to have occurred nearer to the equator than Lat. 40°.

It is important to note that glaciation was not limited to the Australian continent in Upper Palæozoic times ; similar glacial deposits of this age are also found in Africa and South America over large areas, and in the Northern Hemisphere extensive deposits have been found in India, while limited deposits occur in the United States near Boston, and also in England and Germany in Europe. The Upper Palæozoic refrigeration of the climate was therefore worldwide, but the areas affected by the glaciation appear to have been much more extensive in the Southern than in the Northern Hemisphere.

The Triassic and Jurassic Periods.

The available evidence suggests that during these two periods the geological history was very similar and it will be convenient therefore to consider them together.

At the close of the Permian period important earth movements took place which brought about a general uplift of the land of moderate amount, accompanied by a complete retreat of the epicontinental seas which had covered such large areas during the Permian period. As a result, at the beginning of the Triassic period the Australian continent extended further seawards in most parts than it does today. This was particularly the case along its eastern margin, where it extended some considerable distance across what is now the Tasman Sea ; this eastern extension, which has since disappeared beneath the sea, has been called Tasmantis.

Some of the Permian fresh-water lakes in which the Upper Coal Measures had been deposited still continued as such into the Triassic period, and new lakes developed ; thus by the beginning of the Jurassic period very extensive areas in eastern Australia were covered by such lakes. The largest of these has been called Lake Walloon ; it extended from the coast in south-eastern Queensland, westward into central Australia, covered parts of northern New South Wales and extended from there northwards to the present Gulf of Carpentaria ; its area must have been at least 300,000 square miles. In these Triassic-Jurassic lakes a fairly thick series of fresh-water strata was deposited and in many places valuable coal seams are included, such as the Ipswich coal measures of Queensland and the Gippsland Coal Measures of Victoria. The fresh-water strata have yielded an abundance of fossil land plants, as well as fossil insects, Amphibia, fish and reptiles. Many fossil insects have been obtained at Ipswich in Queensland, including many dragon-flies ; they have been described by R. J. Tillyard, and from their nature and the large size of many of them he inferred that they indicated a warm climate. The remains of reptiles found in Queensland belong to an extinct group of large individuals called Dinosaurs, and these also indicate at least a mild climate ; one of these, *Rhœtosaurus*, was about 40 feet in length.

No marine strata of Triassic or Jurassic age have been found in Australia, except a limited area of Jurassic marine strata in north-west Australia. The evidence of the land animals and plants found, however, suggests that the climate during these two periods was at least as warm as, and probably warmer than, it is today. This is supported by the evidence from the Northern Hemisphere, where in Upper Triassic times coral reefs extended into Alaska (Lat. 60° N.), some 2,000 miles north of the present day limit of reef-building corals. While the evidence from the Northern Hemisphere in general suggests a warm climate, it also indicates that some marked oscillations took place, but it was never very cold. Professor Neumayer, of Vienna, as a result of his study in 1883 of a group of cephalopods called the Ammonites and their distribution, concluded that the earth in Jurassic times had clearly marked equatorial temperate and cool polar climates, agreeing in the main with the present occurrences of the same zones.

The Cretaceous Period.

At the close of the Jurassic period an invasion of the sea took place from the north and converted most of the area previously occupied by Lake Walloon into an arm of the sea. This extensive epicontinental sea extended southwards into northern New South Wales and south-westwards into northern South Australia ; it possibly extended also as far southwards as the Great Australian Bight and thus completely divided the Australian continent into two parts This sea brought with it an abundant marine fauna, now found as fossils in the strata deposited in it. From a study of these fossils F. W. Whitehouse has concluded that the water was comparatively cold, his reasons being as follow :

(1) The fauna contains no reef-building corals, no Rudistid lamellibranchs, no equatorial types of Ammonites, and no large types of Foraminifera.
(2) Angular fresh felspars occur throughout the Roma and Tambo series of the Lower Cretaceous.
(3) Ice-borne erratics, some of which show faint glacial striæ, occur as dropped boulders indenting the underlying Cretaceous shales at Stuart Range in South Australia and at White Cliffs in New South Wales.
(4) Pseudomorphs in opal after glauberite are numerous at White Cliffs ; these resemble the Glendonites associated with glacial erratics found in the marine sediments of the Middle Permian of New South Wales.

This evidence of cold climate receives support from the finding of terrestrial glacial deposits in South Australia by W. G. Woolnough and T. W. E. David.[8] These deposits occur in the Flinders Range between latitudes 26° 25′ S. and 30° 25′ S., that is near the southern margin of the Cretaceous sea ; they have been traced over an area of about 40,000 square miles.

E. J. Kenny has recorded the presence of glacial erratics in the Lower Cretaceous marine strata of the Tibooburra district of New South Wales, where they are associated with typical marine fossils of that age.

The existence of probable glacial beds of a similar age has been reported from Great Britain, Iceland, Spitsbergen and South Africa, so that a cold climate appears to have been worldwide at this time ; it is not considered, however, that it was so pronounced as that of Upper Palæozoic time.

The Tertiary Period.

The first three subdivisions of the Cainozoic era, which are called the Eocene, Miocene and Pliocene periods respectively, are frequently grouped together and referred to as the Tertiary period ; and we will follow that practice here.

At the close of the Cretaceous period important earth movements took place which appear to have brought about a complete disappearance of the

epicontinental seas and fresh-water lakes which had covered such large areas in that period. Just what happened during the Eocene period we do not know, as no rocks of this age have yet been found in Australia. Towards the close of the Eocene period a subsidence began in the southern parts of Australia accompanied by considerable transgression of the sea along the present southern margin of the continent ; this subsidence continued throughout the Miocene and

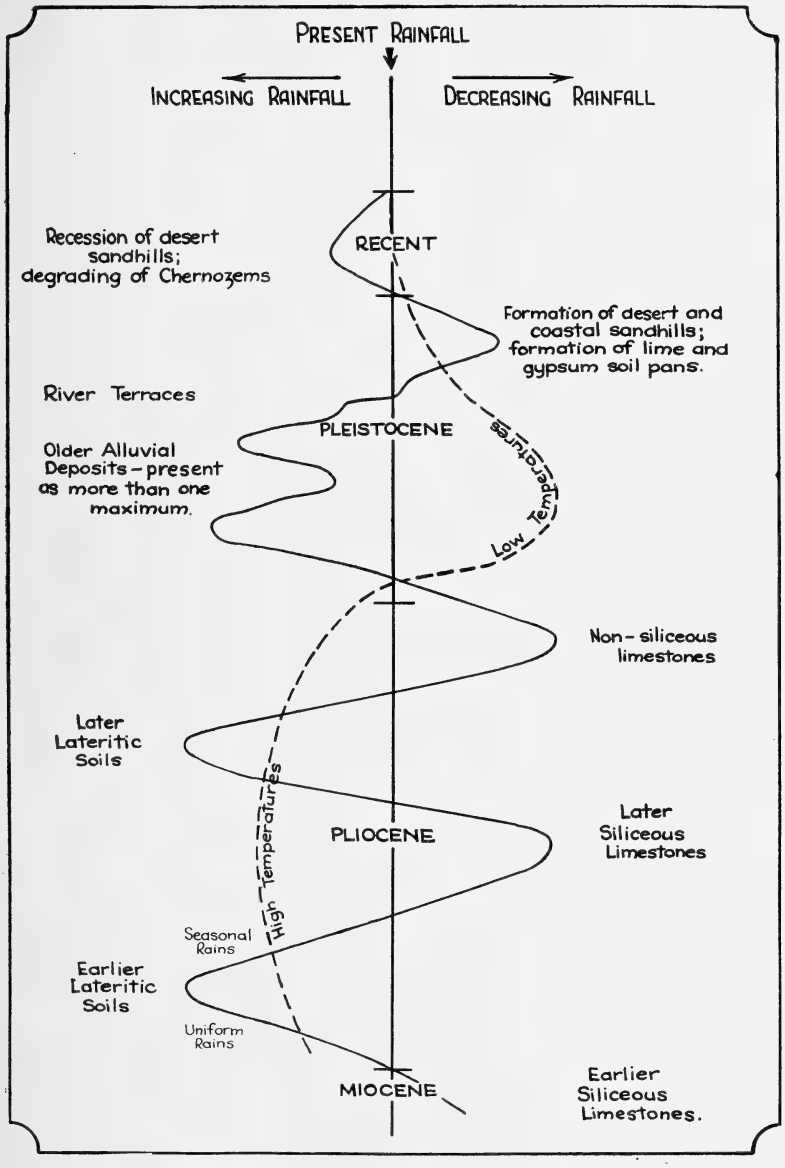

Fig. 3. Generalised curves to interpret the more important climatic changes in Queensland since Miocene times. The centre line represents present-day conditions. The continuous curve assesses rainfall values. The broken line is a general temperature curve. In both curves the cusps to the left represent values higher than at present ; cusps to the right are lower values.

(After Whitehouse.)

Pliocene periods and considerable thicknesses of marine strata were deposited. These strata contain an abundance of marine fossils, mostly polyzoa and mollusca ; some fragmentary remains of whales and sharks have also been found. Reef-building corals are rare, but one genus has been found in the Miocene strata of Table Cape in Tasmania, and from this occurrence T. W. E. David[2] has suggested that the sea there must have been at least 10° F. warmer than it is today, and states further that towards the close of the Pliocene period the evidence suggests that the seas were getting steadily colder.

Fresh-water deposits, mainly river deposits, of Miocene and Pliocene age have been found at many localities in the eastern half of Australia, extending from Queensland to Tasmania and as far west as South Australia, and many of these fossils appear to be very closely related to, and in some cases " identical " with, plants occurring in our present day " brush " forests (rain-forests), now growing in those eastern parts of Queensland and New South Wales where there is a fairly hot climate with a high rainfall. The wide distribution of this type of vegetation in Tertiary time suggests, therefore, a warm moist climate as far south as Tasmania and extending westwards into regions which are now too arid to support such a vegetation. The evidence both from the marine animals and the land plants therefore indicates a climate somewhat warmer and certainly moister than that of today, and this view is supported by evidence from other parts of the world. Possibly in Upper Pliocene times a cooling of the climate began which culminated in the great ice age of the following Pleistocene period.

In Text-figure 3 is shown a diagram prepared by Dr. F. W. Whitehouse showing oscillations of the climate of western Queensland extending from the Miocene period down to the present day ; this is based on variations in the nature of the rocks and soils formed during the periods represented. It shows variations in rainfall as well as temperature, but the curves representing the rainfall do not seem to have any definite relation to the general curve representing the temperature.

The Pleistocene Period.

Very pronounced earth movements took place in Australia at the close of the Tertiary period as a result of which our present mountains and tablelands were elevated to their present positions. Prior to this uplift most of the continent appears to have been low-lying with only occasional isolated hills and short narrow ridges rising above the general level. The production of that great belt of tablelands (the Australian Cordillera) which now exists along the whole of the eastern margin of the continent, and ranges up to 4,000 feet or more in altitude, must naturally have had some modifying influence on the climate locally, but this could not have had any very profound influence on the climate of Australia as a whole. Similar mountain-making movements took place simultaneously in many other parts of the world, and such great mountain ranges as the Alps, Himalayas, Rocky Mountains and Andes were elevated at this time.

Following soon after this great mountain-making epoch, but not necessarily resulting from it, there developed a very pronounced refrigeration of the climate throughout the world, which produced one of the world's great ice-ages. Great ice-sheets came into being, ultimately covering some 12,000,000 square miles of the earth's surface ; in Europe these extended southwards to London and Berlin, and in North America southwards to Cincinnatti in the Mississippi Valley. Glaciation occurred also in the Southern Hemisphere and affected considerable areas in South America, New Zealand and Australia. During this glacial period a considerable lowering of the snow-line took place which varied in amount from place to place, but which averaged about 4,000 feet.

The area submerged under ice in Australia was quite small. About one-half of Tasmania was covered and on the west coast the glaciers extended almost down to sea-level, and the ice ranged up to 1,500 feet in thickness; peat beds occurring in some of the tillites suggests interglacial epochs. On the continent of Australia the glaciation was limited to the small area of the Kosciusko Table-land which projects above the 5,000 feet level. The snow-line in this region is today at an elevation of about 8,000 feet, and in Pleistocene times it was lowered to about 5,000 feet; no other part of the mainland reaches this elevation, apart from the tops of a few isolated peaks, and these are too small in area to have allowed of sufficient accumulation of snow to form glaciers. T. W. E. David states that in the Kosciusko region[2] a small ice-sheet formed early in Pleistocene times, and towards the end of the period, as the cold became less intense, this split up into small valley glaciers, and these finally disappeared not less than about 20,000 years ago.

The reason why Australia, as a whole, was so little affected by the Pleistocene glaciation is that it does not project sufficiently far to the south. In the Northern Hemisphere all the areas glaciated, except some of the high mountains, lay on the poleward side of Lat. 40° N., whereas in Australia the only part lying on the poleward side of the corresponding south latitude is Tasmania.

Because of the very much larger area occupied by the ice-sheets in Europe and North America, these regions display a much more complete record of the glacial conditions than Australia. The Alpine region of Europe gives evidence of at least four distinct advances of the ice, separated from one another by very definite interglacial epochs during which the climate was at least as warm as, perhaps a little warmer than, it is today.; one of these interglacial epochs continued for such a long period of time that the ice-sheets may have almost entirely disappeared for a considerable period of time, only to advance again, however, during the next glacial epoch. In North America there were no less than five separate advances of the ice-sheets.

Various estimates have been made as to the length of time occupied by the Pleistocene ice-age; these estimates vary from 300,000 years to 1,000,000 years. A. P. Coleman[1] gives as his considered opinion a period of from 600,000 to 700,000 years, and also concluded that the last ice-sheet began to retreat some 25,000 to 35,000 years ago.

Two large areas are today still submerged under great ice-sheets; these are the Antarctic continent and the island of Greenland, representing an area of nearly 6,000,000 square miles; many of the high mountain ranges also support large glaciers. In all of these regions the ice today is steadily retreating. Both Antarctica and Greenland have had mild climates in past geological periods and consequently some geologists consider that the great ice-age is not yet finished, and that at the present time we are living in an interglacial epoch.

In some of the Pleistocene terrestrial deposits of Australia there have been found the bones of some extinct marsupials some of which were much larger than any living representatives of this group of vertebrate animals. These have been found not only in the coastal regions where there is today a relatively good rainfall, but also in some of the very arid regions of Central Australia. From Lake Calabonna in the northern part of South Australia almost complete skeletons of an extinct marsupial, Diprotodon, somewhat like a wombat in general form but almost as large as a rhinoceros, have been found; and for herds of these large slow-moving animals to have existed these regions must have had a much better rainfall then than they have now.

Summary.

From the evidence given it will be obvious that very marked changes in the climate of Australia have taken place since the beginning of geological

time ; the more important of these are shown diagrammatically in Fig. 1. On the right-hand side of this diagram the vertical line indicates the present-day climate, while the dotted line indicates the variations, the curves to the left indicating the colder periods, whereas those to the right indicate the warmer periods. It will be noticed that very definite colder periods occurred during (*a*) the Upper Proterozoic era, (*b*) the Carboniferous-Permian periods, (*c*) the Cretaceous period, (*d*) the Pleistocene period. It is worthy of note that each of the great glaciations occurred at or near the close of the Proterozoic, Palæozoic, Mesozoic and Cainozoic eras respectively. On the other hand the definitely warmer periods, which were relatively longer, appear to have started at the beginning of each era and continued through several periods until interrupted by the oncoming colder period towards the close of the era. These facts suggest that the average climate of the past has been warmer than that of today.

The changes of climate shown in this diagram may be referred to as the major ones ; in addition there were changes of a second order, such as the interglacial epochs which took place, for example, during the Carboniferous-Permian glacial period, each of which must have lasted quite a long time. There were oscillations also of a third order, such as those indicated in the diagram in Fig. 3, and superimposed on these again may have been even less important changes.

Another feature that should be noticed is that the climatic changes which Australia has suffered appear to correspond in general with those which occurred simultaneously in other parts of the world, indicating a control which was worldwide in its operation.

It is not proposed to discuss here the possible causes of these changes of climate ; many theories have been advanced, but none have yet met with general acceptance, and it may be said that this is still one of the unsolved problems of geology.

Acknowledgment.

I desire to thank the University of Queensland for permission to make use of text-fig. 3, prepared by Dr. F. W. Whitehouse.

References.

(1) Coleman, A. P. : Ice Ages, Recent and Ancient. Macmillan and Co., London, 1926.

(2) David, T. W. E. : Explanatory Notes, Geological Map of Australia, Australasian Medical Publishing Co. Ltd., Sydney, 1932.

(3) David, T. W. E., and Sussmilch, C. A. : Upper Palæozoic Glaciations of Australia, *Bull. Geol. Soc. of America*, Vol. 42, p. 481.

(4) Howchin, W. : Geology of South Australia. R. E. E. Rogers, Government Printer of South Australia, 1918.

(5) Mawson, D. : The Munyallina Beds, a Late Proterozoic Formation, *Trans. Roy. Soc. of S. Aust.*, Vol. LVIII, 1934.

(6) Whitehouse, F. W. : The Climate of Queensland since Miocene Times, University of Queensland, Department of Geology, Vol. 2, No. 1, 1940, p. 62.

(7) Woolnough, W. G. : The Geology of Flinders Range in the Neighbourhood of Wooltana Station, *Journ. Roy. Soc. of N. S. Wales*, Vol. LX, 1926.

(8) Woolnough, W. G., and David, T. W. E. : Cretaceous Glaciation in Central Australia, *Q.J.G.S.*, Vol. LXXX, Part 3, p. 322.

AN EXAMINATION OF THE ESSENTIAL OILS DISTILLED FROM THE TIPS AND NORMAL CUT OF *EUCALYPTUS POLYBRACTEA*.

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The examination of the oils obtained by monthly distillation of (*a*) growing tips and (*b*) old leaf of *E. cneorifolia* showed marked differences between the two series (Berry, Macbeth and Swanson, *J.C.S.*, 1937, 1443). The yield of oil from the growing tips increased during the period of active growth, accompanied by a pronounced increase in terpene content, while oils from old leaf showed only slight variation from month to month. The association of *l*-α and *l*-β phellandrene in (*a*) with *l*-phellandral, *l*-4-isopropyl-$\triangle^2$-cyclohexen-1-one (termed cryptone, *J.C.S.*, 1938, 1409) and cuminal was discussed in connection with the biogenetic relationship of these constituents.

Since *E. polybractea* has been shown to contain the same three carbonyl constituents (Penfold, *J.C.S.*, 1922, *121*, 266 ; Cahn, Penfold and Simonsen, *ibid.*, 1931, 1366 ; Berry, Macbeth and Swanson, *ibid.*, 1937, 986), it was decided to examine oils distilled monthly from the tips of this species and also from the normal growth, to see if a similar relationship occurred. Messrs. J. Bosisto & Co. Pty. Ltd. kindly collected the material and carried out the monthly distillations of the oils (Tables I and II).

Only slight differences occurred between the two series. The variations in the monthly oils from the young tips were remarkably small ; alcohols ranged from 1·9% to 5·6%, aldehydes and ketones from 2·2% to 3·7%, cineole from 87·2% to 92·0%, and terpenes, etc., from 2·2% to 7·2%. No evidence of a seasonal variation in the composition of the oils from the young tips was apparent. Unfortunately, the climatic conditions during the period of the investigation were most unfavourable and undoubtedly adversely affected the formation of oil. It is during the months October to January that the most pronounced variations in the oils are likely to occur. The rainfall for the year 1938 was only 7 inches (average annual 17·87 inches), while the excessively hot summer of the year 1938-1939 was also an important factor. One leading distiller recorded that the drought had caused the leaves to wither and turn yellow. We hope at a later date to examine the oils over a normal season and see if any appreciable variation occurs in the oils from the growing tips.

It was decided, however, to carry out a more detailed investigation of several samples of the oils to see if relevant differences could be observed and to identify the aldehydes and terpenes present.

The results of a detailed examination of four of the samples of oil have been summarised in Table III.

In the oils examined, the high boiling carbonyl constituents have been identified as a mixture of *l*-phellandral, *l*-cryptone (*l*-4-isopropyl-$\triangle^2$-cyclohexen-1-one) and cuminal. Insufficient material was obtained for the accurate estimation of the relative proportions of cuminal, cryptone and phellandral. The total amounts recovered varied from 25% to 60% of the amount present as indicated by the hydroxylamine estimation. Associated with these carbonyl

TABLE I.

Analyses of the Crude Oils Distilled from the Tips only of E. polybractea.

Reference Number.	Leaves Cut.	Leaves Distilled.	Percentage Yield.	Specific Gravity 15·5/15·5.	Specific Rotation $[\alpha]_D$.	Ester Value.	Total Alcohols Calculated as $C_{10}H_{18}O$.	Total Aldehydes and Ketones Calculated as $C_{10}H_{14}O$.	Cineole by O-Cresol Method.	Terpenes, etc., by Difference.
							%	%	%	%
2	30/3/38	4/4/38	2·21	0·9270	+0·90	6·3	3·3	2·2	87·3	7·2
4	27/4/38	29/4/38	1·77	0·9276	+0·32	7·0	5·6	2·8	87·2	4·4
6	25/5/38	30/5/38	2·34	0·9272	+0·28	8·8	4·2	3·7	87·4	4·7
8	29/6/38	1/7/38	1·61	0·9279	+0·26	9·8	3·9	3·4	88·0	4·7
10	27/7/38	1/8/38	1·67	0·9285	+0·11	9·8	4·3	2·9	88·6	4·2
11	31/8/38	2/9/38 } 5/9/38 }	2·09	0·9279	+0·09	8·0	3·9	2·3	89·0	4·8
14	28/9/38	10/10/38 } 11/10/38 }	1·79	0·9290	+0·15	9·1	2·4	2·4	89·2	6·0
15	26/10/38	28/10/38 } 31/10/38 }	1·65	0·9287	−0·02	6·7	2·5	2·5	90·0	5·0
17	30/11/38	2/12/38 } 5/12/38 }	1·12	0·9294	−0·13	4·5	3·6	2·5	91·7	2·2
19	28/12/38	6/1/39 } 9/1/39 }	1·31	0·9294	−0·30	10·5	1·9	2·4	90·4	5·3
22	25/1/39	3/2/39 } 6/2/39 }	1·08	0·9305	−0·52	11·2	1·9	2·3	91·2	4·6
23	22/2/39	3/3/39 } 6/3/39 }	0·82	0·9296	−0·56	7·0	3·3	2·9	91·0	2·8
26	29/3/39	3/4/39 } 4/4/39 }	1·60	0·9291	−0·30	6·3	2·3	2·3	92·0	3·4

TABEL II.

Analyses of the Crude Oils Distilled from E. polybractea, *Normal Commercial Cut.*

Reference Number.	Leaves Cut.	Leaves Distilled.	Percentage Yield.	Specific Gravity 15·5/15·5.	Specific Rotation $[\alpha]_D$.	Ester Value.	Total Alcohols Calculated as $C_{10}H_{18}O$.	Total Aldehydes and Ketones Calculated as $C_{10}H_{14}O$.	Cineole by O-Cresol Method.	Terpenes, etc., by Difference.
							%	%	%	%
1	23/3/38	31/3/38	1·96	0·9244	+0·93	4·9	5·5	2·1	86·8	5·6
3	27/4/38	2/5/38	1·50	0·9272	+0·02	4·9	5·9	2·6	86·9	4·6
5	25/5/38	31/5/38	1·52	0·9278	−0·77	8·8	4·5	4·6	86·2	4·7
7	29/6/38	4/7/38	1·26	0·9272	+0·37	9·1	4·0	3·2	87·2	5·6
9	27/7/38	3/8/38	1·43	0·9285	+0·19	9·1	4·7	2·7	88·1	4·5
12	31/8/38	6/9/38 } 7/9/38 }	1·66	0·9286	+0·04	9·4	3·5	1·9	90·0	4·6
13	28/9/38	6/10/38 } 7/10/38 }	1·95	0·9284	+0·10	6·3	3·6	2·5	89·6	4·3
16	26/10/38	2/11/38 } 3/11/38 }	1·70	0·9291	+0·28	10·2	2·3	2·7	88·8	6·2
18	30/11/38	6/12/38 } 7/12/38 }	1·26	0·9300	+0·02	4·9	4·5	2·6	91·2	1·7
20	28/12/38	10/1/39 } 11/1/39 }	0·88	0·9300	zero	6·3	4·5	2·5	90·7	2·3
21	25/1/39	1/2/39 } 2/2/39 }	1·17	0·9300	−0·13	9·1	1·7	2·2	92·0	4·1
24	22/2/39	7/3/39 } 8/3/39 }	0·96	0·9292	−0·52	9·1	2·3	3·0	90·4	4·3
25	29/3/39	5/4/39 } 6/4/39 }	0·70	0·9295	−0·34	10·5	2·3	2·5	90·4	4·8

Table III.

Oil Number.	Ketone Percentage in Crude Oil. (Actual Recovery.)	Phellandral and Cuminal Mixture (Percentage in Crude Oil.) (Actual Recovery.)	Approximate Percentage of Phellandral in Mixture.	Percentage Terpene and Cymene in Oil. (Actual Recovery.)	Terpene and Cymene Rotation $[\alpha]_D$.	Percentage Cymene in Terpene Fraction.	Percentage Cymene in Oil.
1. Normal cut 23/3/38.	0·52	0·74	5	2·1	+13·3	46·7	1·0
2. Growing tips 30/3/38.	0·59	0·40	12	5·2	+11·5	38·7	2·0
5. Normal cut 25/5/38.	0·90	1·11	34	4·0	+9·0	29·0	1·2
6. Growing tips 25/5/38.	0·50	0·42	6	4·1	+11·8	21·5	0·9

compounds is a dextro-rotatory terpene which has not yet been identified, but which definitely contains no appreciable amount of phellandrene. In this connection it is of interest to note that during the investigation of the oils distilled from the tips of *E. cneorifolia*, dextro-rotatory terpene fractions were obtained from some of the winter oils (i.e. after growth had ceased). These responded only slightly to the test for phellandrene. A further investigation of this terpene will be carried out.

Cymene is present in the oils in association with the terpene and constitutes approximately from 20-50% of the terpene fraction. Some evidence was obtained of the presence of keto-phenols in the oil.

As will be seen from Tables I and II, cineole constitutes approximately 90% of every sample, the range over 26 samples being 86·2% to 92%, a remarkably uniform result. Alcohols were also present, but no further work has been done on them.

Meteorological Data.

Rainfall.

Inglewood, Victoria.

Average Monthly and Annual Rainfall.

(In Inches.)

Years.	Jan.	Feb.	Mar.	April.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Year.
51 years of record	0·97	1·02	1·19	1·30	1·99	2·22	1·73	1·92	1·67	1·48	1·18	1·20	17·87
1937	1·74	0·60	0·19	1·31	1·10	0·67	0·34	1·59	0·96	3·17	0·23	1·13	13·03
1938	0·74	0·56	0·09	0·63	0·21	1·64	1·97	0·57	0·19	0·05	0·36	—	7·01
1939	0·93	4·86	0·40	3·03	2·84	2·53	1·34	2·29	0·93	1·63	3·06	0·32	24·16

Temperature.

Bendigo, Victoria (the nearest town recording these details).

Average Mean Maximum Monthly Temperature.

Years.	Jan.	Feb.	Mar.	April.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Year.
75 years of record	85·4	85·2	79·2	70·0	61·4	55·2	54·0	57·2	62·4	69·2	76·4	81·9	69·8
1937	78·3	84·2	79·9	68·2	60·5	56·4	54·6	60·3	63·2	71·6	80·9	80·0	69·8
1938	82·1	81·7	81·7	73·5	66·4	53·6	53·4	57·2	64·2	74·6	80·2	82·7	70·9
1939	91·6	86·3	77·0	67·8	62·2	53·2	52·0	54·6	60·8	67·0	70·8	77·7	68·4

Experimental.

Distillations.

The distillations were carried out by Messrs. J. Bosisto & Co. Pty. Ltd. at their Richmond factory from material collected at Inglewood (Victoria). The leaves (average weight about 150 lb.) were delivered at Richmond the day after cutting, and the oil distilled as soon as possible by steam distillation. The time of distillation was 3½ hours. The crude oils were analysed without further rectification, cineole being determined by the o-cresol method; alcohols (calculated as $C_{10}H_{18}O$) by difference between the ester value of the oil and the ester value after acetylation; aldehydes and ketones by the hydroxylamine method; and terpenes by difference. Aldehydes and ketones were calculated as $C_{10}H_{14}O$, in conformity with our work on *E. cneorifolia* oils (*loc. cit.*). The ester values have not been calculated in terms of a particular ester, since the individual values are comparatively low; the figures for terpenes, etc., therefore include esters.

Examination of Individual Oils.

As the method of separation and identification of the various constituents was the same for each oil, it will be sufficient to describe the general method, and a typical result.

The following are the results for oil No. 5. The methods used for the separation of the various constituents are described previously (Berry, Macbeth and Swanson, *loc. cit.*).

Crude oil, 1,007 gm. Extracted with 500 ml. of 35% Na_2SO_3. Unabsorbed oil 994 gm. $[\alpha]_D$ −1·2. Ketone recovered 9·0 gm., $[\alpha]_D$ −43°. Identified by preparation of p-nitrophenylhydrazone, m.pt. 168° C. (recryst. from MeOH); m.pt. undepressed by admixture with same derivative of authentic *l*-cryptone (*l*-4-isopropyl cyclohexen-1-one).

The unabsorbed oil, after drying with anhydrous magnesium sulphate, weighed 911 gm., and was then distilled under a pressure of 2 mm., through a 50 cm. rod and disc column with the following result:

Fraction.	Weight.	Temperature.	Pressure.	Specific Gravity. 15°/15°.	Specific Rotation $[\alpha]_D$.
	g	° C	mm		
1	116	40–44	2	0·9227	+1·43
2	468	44–48	2	0·9239	+0·97
3	180	48–49	2	0·9258	+1·08
Still residues ..	130	—	—	0·9649	−1·50
Loss	17				

When treated as described before the still residues gave 7·1 g. of aldehyde A, $[\alpha]_D$ −31·3, and 3·0 g. aldehyde C, $[\alpha]_D$ −40·2. These two aldehydes were mixed in alcoholic solution and treated with boiling 35% sodium bisulphite solution (Penfold's separation). From the solid cake was obtained 4·0 g. aldehyde, $[\alpha]_D$ ±0. This gave a p-nitro-phenylhydrazone m.pt. 192-193° C., recryst. from MeOH, which gave no depression of m.pt. when mixed with an authentic specimen of cuminal p-nitro-phenylhydrazone. The aldehyde oxidised rapidly in air, and after purification and recrystallisation from dil. acetic acid, the acid so obtained melted at 117° C. (cuminic acid).

From the bisulphite solution of the above separation was obtained 3·0 g. aldehyde, $[\alpha]_D$ −66·7°. This gave a 2 : 4 dinitro-phenylhydrazone, m.pt. 201-202° C., recryst. from ethyl acetate; mixed m.pt. with authentic *l*-phellandral derivative showing no depression. The remainder of the aldehyde was oxidised to the corresponding unsaturated acid, m.pt. 144° C., recryst. from aqueous MeOH; $[\alpha]_D$ −103 (c., 2·05 in MeOH), which are the constants for *l*-phellandric acid.

Twenty per cent. of the combined terpene fraction, treated as described before, with the modification that it was mixed with twice its volume of petroleum ether before shaking with resorcinol solution, gave 7·3 g. of terpene and cymene. This had $[\alpha]_D$ +9·0 for the mixture and gave no precipitate in petroleum ether solution when treated with nitrous acid at 0° C.,

thus indicating absence of phellandrene. From this was obtained 2·1 g. of cymene, optically inactive, which on oxidation with hot aqueous potassium permanganate gave the characteristic p-hydroxyisopropyl benzoic acid, m.pt. 156-157° C.

Separation of Phenols, etc.

The crude oil was shaken twice with 40 c.c. of 5% NaOH, and twice with 50 c.c. of water. The combined extracts were shaken with ether to remove adhering oil and then acidified with 3N sulphuric acid in the presence of ether. After drying and removal of ether the alkali-soluble fractions were recovered.

To attempt a separation of these fractions, the above material was dissolved in ether and shaken with 5% sodium carbonate solution (Trikojus and White, *Proc. Royal Soc. N.S.W.*, 1932, *66*, 279). From the ether an oil was recovered, and by acidification and extraction of the sodium carbonate solution in the usual way with ether a second oily fraction was obtained.

Neither fraction as prepared above gave definite colour reactions characteristic of australol (Earl and Trikojus, *Proc. Royal Soc. N.S.W.*, 1925, *59*, 301) or " Tasmanol " (*loc. cit.*) with alcoholic ferric chloride, and an attempt to prepare the benzoate of the portion soluble in NaOH only, yielded a non-crystalline gum.

Both the fraction soluble in sodium carbonate solution and the fraction soluble in sodium hydroxide solution were examined to determine if they contained any of the keto-phenols reported by Reuter (*Jour. and Proc. Aust. Chem. Inst.*, 1938, *5*, 291). It was noticed that the fraction soluble in NaOH gave a blue-green colour with alcoholic ferric chloride and reacted with 2 : 4 dinitro-phenylhydrazine to give a precipitate, m.pt. 125° C. The fraction soluble in sodium carbonate gave no precipitate with the above reagent and appeared to be chiefly a mixture of liquid acids. This result would appear to confirm that of Reuter (*loc. cit.*) that keto-phenols are present in the oil of this species.

We wish to thank Professor A. K. Macbeth, who suggested this investigation, and under whose direction it was carried out; also Bosisto & Co. Pty. Ltd. for collecting the material and distilling the oils.

One of us (T.B.S.) is indebted to the Commonwealth Government for a Federal Research Grant which enabled him to complete the work.

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THE JURASSIC FISHES OF NEW SOUTH WALES.

By R. T. Wade, M.A., Ph.D.

(With Plates II, III and 8 Text-figures.)

(Manuscript received, April 23, 1941. Read, June 4, 1941.)

The Collections.

In 1895 the Geological Survey of New South Wales published a description by Smith Woodward of a collection of fossil fishes from a locality near Talbragar Creek, north of Gulgong, New South Wales.[4] The greater part of this collection and one made by the late John Mitchell are housed in the Australian Museum, Sydney.

In 1936 and 1939, with some financial assistance—now gratefully acknowledged—from the Council for Scientific and Industrial Research, I was able to visit the field and collect not only specimens of most of the recorded species, but also several specimens of a new Macrosemiid.

Locality and Age.

The fossils were found at Farr's Hill, Uarbry Road, about 16 miles from Gulgong, but the beds are best approached from the Mudgee-Cassilis road, through Bobadean Station, situated about 3 miles from Farr's Hill.

The age of the beds is discussed by J. A. Dulhunty.[1]

The Cenogenoidei.

Under this head are grouped the fishes *Ætheolepis*, *Archæomæne*, and *Aphnelepis* of Smith Woodward.[4] He provisionally assigned *Ætheolepis* and *Aphnelepis* to the Semionotidæ, and *Archæomæne* (2 spp.) to the Pholidophoridæ. Goodrich[2] removed *Archæomæne* to a new family, the name of which by transliteration is printed as Archæonemidæ, the genus being termed *Archæonemus* [*sic.*]. Now, however, that the structure of the heads of these genera is known, it is quite clear that none are referable to any of the recognised Holostean families.

The chief reason both for regarding them as a group of related families and for separating the group from the normal Holostei is to be found in the structure of the cheek. This is covered by three bones: a large suborbital adjoining the operculum, a moderately extensive preoperculum, and a greatly expanded circumorbital, which extends backwards from the postero-inferior margin of the orbit to the preoperculum. Of much less importance in itself, but reinforcing the argument from the unusual cheek, is the blending of primitive, Holostean, Holosteo-Teleostean, and Teleostean characters revealed in the systematic description of the species.

While the reference of *Archæomæne* to the Pholidophoridæ can no longer be maintained, *Archæomæne* is very like species of *Pholidophorus* in the shape of the whole fish, the shape of the mouth and of the lower jaw, the shape of the maxillæ and supramaxillæ. The most important respects in which *Archæomæne*

differs from *Pholidophorus* are: (*a*) the scales of *Archæomæne* are cycloid; (*b*) vertebral rings and ossified ribs are found in *Archæomæne*; (*c*) the circumorbital in the cheek of *Archæomæne* covers a large part of that area, but *Pholidophorus* has two very slightly extended circumorbitals.

These differences, however, may well be regarded as developments of, or advances beyond, the Pholidophorid structure, in which case it would be reasonable to conclude that the Archæomænidæ are derived from a Pholidophorid stock.

The resemblance of *Ætheolepis* and *Aphnelepis* to *Archæomæne* in the structure of the cheek and some other characters would associate them with *Archæomæne* as derived also from the Pholidophoridæ, while to support this view of the origin of *Ætheolepis* there is added the resemblance of the lower jaw of *Ætheolepis* to that of *Leptolepis*, a genus which is usually regarded as proceeding from the Pholidophoridæ.

It might be inferred, then, either that the three families are derived from a common species of *Pholidophorus*, and have separated from each other as a result of adaptive radiation, or that they were separately derived from closely allied species of *Pholidophorus*. The first inference would rely on the great plasticity which piscine structures display under environmental pressure; the second on the known unevenness in the structural characters of the Pholidophoridæ, into which in the past many species have been dumped on very scanty evidence.

Thus we seem provided at the emergence of the Teleostei with a set of structural conditions parallel with those at the emergence of the Holostei. At the end of the Permian epoch and beginning of the Triassic there were: (1) persistent Palæoniscidæ; (2) species of sub-Holostei which retain much of the Palæoniscid structure but exhibit advance in one or more particulars to the Holostean condition; (3) a true Holostean. Likewise, here, early in the Jurassic, there are, together with the earliest of the Teleostei (Leptolepis): (1) Palæoniscidæ, now somewhat Teleostean (*Coccolepis* with cycloid scales); (2) Holostei; (3) the Cenogenoidei, exhibiting some Teleostean characters—an example of convergent evolution similar to that evident in the mutual relations of sub-Holostei and Holostei.

In all three orders—Chondrostei (*Coccolepis*), Holostei (e.g. *Archæomæne*), Teleostei (e.g. *Leptolepis*)—the change occurred contemporaneously from ganoid to cycloid scales, as though this alteration in genetic constitution were a function of time.

LETTERING USED IN TEXT-FIGURES.

Clei.	Cleithrum.	Pas.	Parasphenoid.
C.O.	Circumorbital.	pl.	"Pitline."
Fr.	Frontal.	P.Mx.	Premaxilla.
Gu.	Gular plate.	P.Op.	Preoperculum.
I.Op.	Interoperculum.	P.Op.C.	Pre-opercular canal.
Lac.	Lachrymal.	P.Ros.	Post-rostral.
L.L.C.	Lateral line canal.	P.T.	Post-temporal.
Md.	Mandible.	R.Br.	Branchiostegal rays.
Md.C.	Mandibular canal.	S.Clei.	Supra-cleithrum.
Md.Sym.	Mandibular symphysis.	S.Mx.	Supra-maxillary.
Mx.	Maxilla.	S.O.	Suborbital.
Na.	Nasal.	S.O.C.	Supraorbital canal.
Op.	Operculum.	S.Op.	Subopercular.
Orb.	Orbit.	S.T.	Supratemporal.
Pa.	Parietal.	Tab.	Tabular.

Order HOLOSTEI.

Sub-Order CENOGENOIDEI.

Small fishes having eye large, cheek covered by preoperculum, large circumorbital, and one large suborbital; supraorbital sensory canals ending back in frontals or in parietals. Vertebræ not constricted; ribs ossified; scales ganoid, or ganoid together with cycloid, or cycloid with trace of ganoine. Other known characters Holostean.

The name, from *kainos*, new, and *genus*, cheek, refers to the approach made in the structure of the cheek to the Teleostean condition of that area.

Family Archeomænidæ.

Diagnosis. Small fishes having fusiform bodies that may be deep. Snout obtuse. Upper fleshy lobe of tail moderately produced; caudal fin forked. Suspensorium slightly inclined forwards; gape small, teeth minute. Bones of head smooth or very faintly ornamented. Scales smooth, nearly cycloid. Fins small; median fins may be of moderate size.

Notochord persistent, ring vertebræ feebly developed or absent. Ribs long, slender; ribs, neural and hæmal arches and spines superficially calcified.

Premaxillæ small, triangular; median postrostral small; nasals large, irregular. Frontals large, not greatly excavated over orbits, wide behind orbits, narrowed greatly between upper ends of nasals; parietals large, quadrangular; tabulars triangular, placed behind parietals and supratemporals; supratemporals of moderate size, irregular. Circumorbital series of more than seven bones, one of which extends well over cheek. One large suborbital much deeper than long; preoperculum arcuate, extending forwards ventrally. Operculum much larger than suboperculum; interoperculum small, triangular; branchiostegal rays few or moderately numerous; median gular large, triangular. Maxillæ long, tapering greatly anteriorly; supramaxillæ small. Mandible long, not greatly deepened in coronoid region, tapering gently anteriorly.

Fin rays with long proximal joint, branched and divided into small joints distally; fulcra small. Scales smooth, thin, almost cycloidal; thicker and overlapping to give appearance of rhombic scales on anterior flank; not deepened on flanks.

Genus Archæomæne Woodward, 1895.

Diagnosis. Small Archæomænidæ having "gracefully fusiform" bodies. Fins small, fin rays somewhat delicate. Circumorbital bones of symmetrical shapes; circumorbital which extends over cheek of moderate size only. Preoperculum of nearly uniform width except at tapered lower end. Branchiostegal rays fairly numerous. Cleithrum arcuate, bent forwards ventrally beneath branchiostegal rays; supracleithrum deep, with expanded head. Supraorbital sensory canals ending back in parietals. All fins small; pectoral with about ten rays, pelvic five or six, dorsal at least ten, anal about fourteen.

Genotype. *Archæomæne tenuis* Woodward.

Archæomæne tenuis Woodward.

(Pl. II; Text-figs. 1, 2, 3, 4.)

Diagnosis. As for genus.

Holotype. A nearly complete fish, No. 69, the original of Plate II, fig. 5, Woodward,[4] in the Mining Museum, Sydney.

Material. The holotype and seven specimens, Nos. MF. 761, MF. 257, MF. 258, MF. 259, F. 39292, F. 39293, F. 27070, in the Australian Museum, and several specimens in my own collection.

Head. The head, which is comparatively small, is about as deep as long. The orbit is large, placed well forward and centrally. The suspensorium is slightly inclined forwards. Both mandible and maxilla are moderately long, but the gape is small.

The structure of the snout is clearly displayed in specimen No. F. 39292 (Pl. II, fig. 1 ; text-fig. 1). Small, triangular, dentigerous premaxillæ, of little depth, are surmounted by a postrostral, the greater part of the area of which extends as a triangle between the lower margins of nasals of moderate size, which meet above the postrostral in a short line of contact in the mid-line of the head.

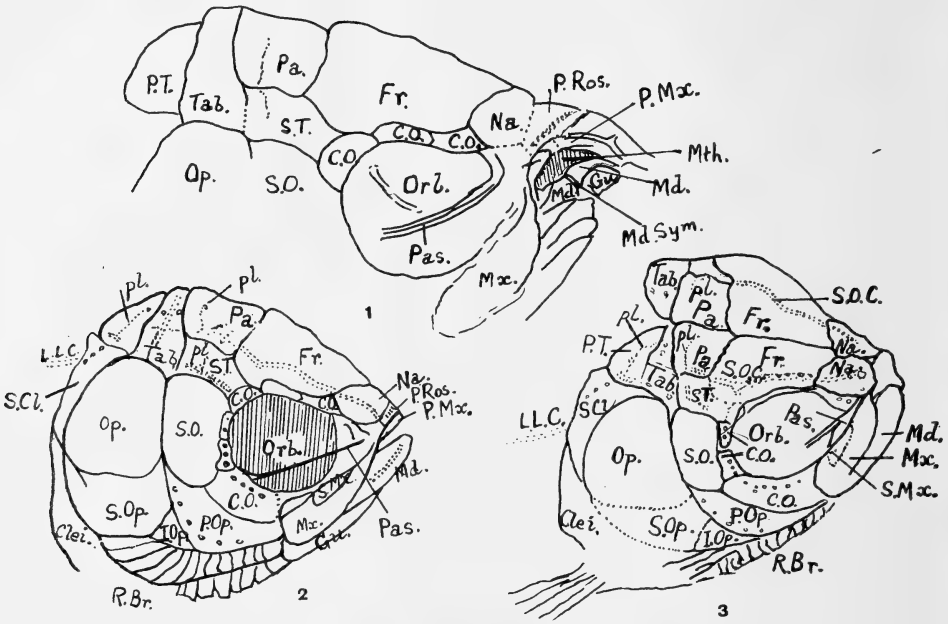

Fig. 1. *Archæomæne tenuis.* Part of head, especially the snout, from Austr. Mus. No. F. 39292. ×5/2.

Fig. 2. *Archæomæne tenuis,* head. Composite drawing based on Austr. Mus. No. MF. 761. ×7/4.

Fig. 3. *Archæomæne tenuis.* Head, especially cranial roof, based on Austr. Mus. No. F. 39293. ×5/2.

The cranial roof may be determined in several specimens. The frontals, the line of junction of which is nearly straight, are about half as wide again posteriorly as in front, are very slightly excavated above the orbits, and are well rounded at the outer corners of their hinder margins. On the mid-line of the head they narrow and project for a short distance between the nasals. The parietals, which are quadrangular, are a little longer than wide, with gently sinuous margins. There are large triangular tabulars, their width much greater than their length. The supratemporals are large bones, the posterior margins concave and the outer margins nearly straight. Their lines of contact with the parietals and the frontals are sinuous, and they are concave in front where they meet the circumorbitals.

The circumorbital series is well defined except below the orbit. In MF. 761 (Text-fig. 2), for example, there is at the top of the back of the orbit a large bone, concave on the orbital side, rather narrow where it meets the frontal and deeper

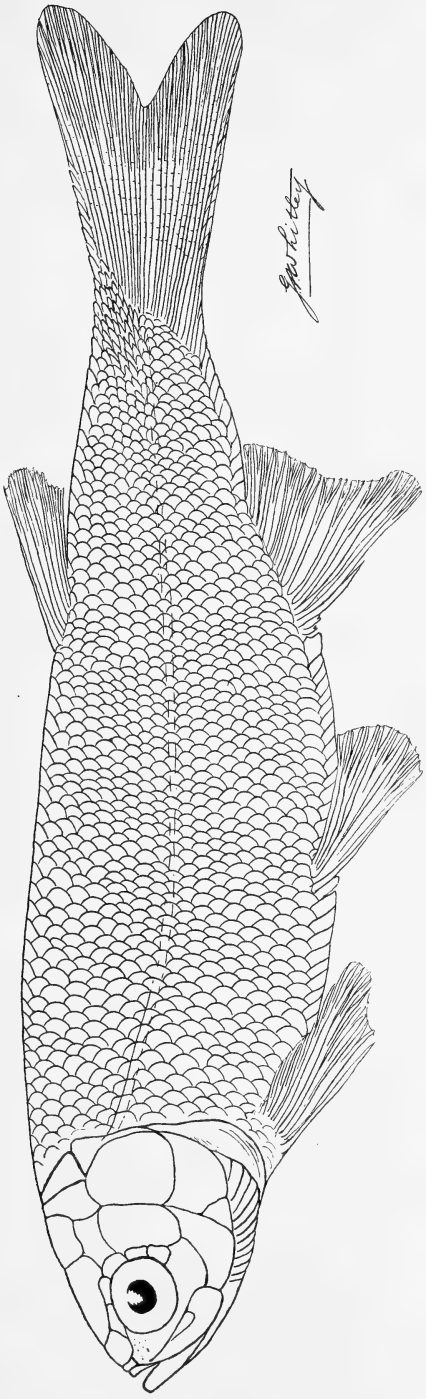

Fig. 4. *Archæomæne tenuis*. Restoration based on the holotype and figures by Smith Woodward and R. T. Wade.
G. P. Whitley, del.

at its contact with the supratemporal. Extending forwards from this along the top of the orbit there is a long narrow bone, which is followed by a similar but narrower bone extending over much of the top front of the orbit to the nasals. Behind the orbit are two circumorbitals of nearly equal size, and bordering the back half of the lower edge of the orbit there is a bone almost equal in area to the exposed surface of the preoperculum. Extending from the supratemporal behind the circumorbitals to nearly the depth of the orbit is a large suborbital, which is about half as long as it is deep.

The operculum is roughly quadrangular, slightly longer in its lower than its upper sections and little deeper than long. The subopercultum, which is much smaller than the operculum, has a short anterior margin and well rounded hinder margin, and the exposed area at the top corner between operculum and preoperculum is very acutely triangular. There is a small triangular interoperculum. The preoperculum is of considerable area, irregularly concave at the top where it receives a suborbital, having its hinder margin greatly bent near the bottom of the bone.

About eight short strap-like branchiostegals lie below the preoperculum and some longer rays lie beneath the opercular series.

The mandible, which is of moderate length, deepens little in the coronoid region, and from that point tapers only slightly to the front. The maxilla, with one small lenticular supra-maxilla fitted into its upper surface, is much longer than deep and tapers greatly forwards.

Much of the system of sensory canals is well preserved as casts or impressions of the canals or casts of the tubuli. The course of the lateral line entering the supracleithrum is marked by tubuli and a channel; a small segment of the canal turns back into the post-temporal, but tubuli alone show its position in the tabular and supratemporal. Specimen F. 39293 (Pl. II, fig. 2; Text-fig. 3) preserves the post-orbital branch in two circumorbitals behind the eye and a specimen in the author's collection displays a calcite cast with small branches running around the orbital margin of the largest circumorbital. From the parietals a "pit-line" extends into the supratemporals, and near the lower anterior corner of the parietals there is a short cast which seems to lead into the well defined channel which traverses frontal and nasal. Specimen F. 39292 (Pl. II, fig. 1; text-fig. 1) preserves the cast of the canal which crosses the snout in the post-rostral. In the preoperculum the course of the canal is marked by casts of the tubuli, and there is in addition near its upper anterior corner the cast of a short pit-line.

Genus **Madariscus**, gen. nov.

Diagnosis. Small Archæomenidæ having moderately deepened bodies. Finrays stout, well spaced. Circumorbital bones of irregular size and shape, fairly wide; one extending well over cheek. Preoperculum rather long mesially. Branchiostegal rays few.

Genotype. *Archæomœne robustus* Woodward, 1895.

Madariscus robustus (Woodward).

(Pl. III, fig. 2; text-fig. 5.)

Diagnosis. As for genus.

Holotype. An imperfect fish in the Australian Museum, No. MF. 250 (Woodward,[4] Pl. V, fig. 2).

Material. The holotype and specimens numbered as follows: MF. 250, MF. 252, MF. 255, MF. 256, all in the Australian Museum.

Head. This is a little longer than deep. The orbit, which is large, is placed centrally and well forward. The suspensorium lies obliquely to a degree

that places the hinder end of the mandible well in advance of a line through the back of the orbit. The gape is small. In the greatly crushed snout (MF. 256, Pl. III, fig. 2 ; text-fig. 5) a fragment only of a post-rostral is preserved, but large nasals of irregular shape can be almost completely delimited.

The frontals are large, but greatly broken on their inner margins in the only specimen (MF. 256), which displays them well. Along the mid-line they project downwards for some distance between the nasals, which thereafter meet one another. Although the frontals are wide behind the orbits, they are not greatly narrowed above them. Their hinder margins are sinuous, being concave where in contact with the parietals and having a pronounced sweep forwards as they leave contact with the parietals. The parietals are small, quadrangular, slightly wider behind than before, and slightly longer at their inner than at their outer margins, while all margins are gently sinuous. Quadrangular tabulars, much wider than long, meet in short lines of contact which are much shorter than their outer margins. The supra-temporals, of moderate size, are irregular, having the anterior and posterior margins concave where they meet the frontals and tabulars respectively, and their inner and outer margins slightly sinuous where they are in contact with the parietals and suborbitals.

The orbit is bounded by nine or ten bones of irregular size and shape. A bone which is probably a lachrymal, with its hinder end on the lower front margin of the orbit, tapers forwards for a length that is about three times its greatest depth. Two bones of irregular outline together with the lachrymal complete the front margin of the orbit. Nearly the whole upper border is formed by one large quadrangular bone, the convex inner margin of which occupies nearly the whole of the frontal's supraorbital concavity. Three small bones, nearly as deep as wide, bound the hinder margin, and one conspicuously large quadrangular bone lies between the preoperculum, where its margin is convex, the orbit, the lower suborbital, and the back of the maxilla.

One large suborbital bone of irregular shape lies between the operculum and the circumorbital ring. The opercular plates are well preserved. The operculum, which is about one and a half times as deep as long, is about three times as deep as the suboperculum. Its hinder margin is concave and as this is traced upwards it sweeps forward, reducing the width of the upper margin of the operculum to about one-third of the width of its lower margin.

The front upper corner of the quadrangular suboperculum displays an acute angle between the operculum and preoperculum. There is a small triangular interoperculum. The preoperculum, which is comparatively large, is widest about its middle, where it is bent to such an extent that hinder and lower margins meet in a right angle with its apex rounded off.

There were more than a dozen branchiostegal rays on either side, and a very large median gular.

The maxilla, which is of moderate length, is deepest near its hinder end and less than three times as long as deep. The lower margin is gently convex ; the upper margin is excavated to less than half its depth by a concave niche, which is occupied by a pair of supra-maxillæ of greatly unequal size. The mandible, which is of moderate length, is only slightly deepened at the coronoid area and tapers gently forwards. Triangular post-temporals join the head to large supra-cleithra which are much deeper than long, and are longest at their upper ends.

The sensory canals are not well preserved except in the nasals and pre-operculum. A " pit line " crosses the supratemporal obliquely.

The name *Madariscus*, derived from *madaros*, bald, refers to the lack of ornament on the head bones ; but it is likely that what is preserved is the inner surface of the bones, for the cleithra and supra-cleithra are ornamented by short, coarse, irregular rugæ.

Family Aphnelepidæ.

Diagnosis. Small fishes having moderately deep fusiform bodies. Snout pointed, tail with slightly produced upper fleshy lobe, caudal fin forked. Suspensorium inclined slightly forwards. Gape wide, teeth small, stout, conical. Orbits of moderate size. Bones of cranial roof and upper part of operculum and suborbitals ornamented with numerous tubercles and short irregular rugæ, arranged in part parallel to margins of bones. Scales highly ornamented in hinder halves by transverse rugæ. Median fins of moderate size; paired fins much smaller.

Notochord persistent; hypocentra and pleurocentra in caudal region; ribs long.

Premaxillæ small, triangular; post-rostral of moderate size; nasals large, irregular. Frontals large, narrow between, wide behind orbits; parietals nearly square; tabulars triangular, extending behind parietals and supratemporals; supratemporals of moderate size, irregular. Three small circumorbitals bordering frontals; one large circumorbital extending over cheek; one large suborbital between operculum and orbital margin; lachrymal of moderate size, leaf-like.

Preoperculum large, moderately wide dorsally, bent forwards ventrally. Maxilla much longer than deep; two small supra-maxillæ. Mandible deep in coronoid region, tapering forwards, with slight droop anteriorly; articular, surangular, and dentary elements at least. Operculum quadrangular, much deeper than long; subopercular much smaller than operculum; interopercular small, triangular, placed almost in front of subopercular. Branchiostegal rays not numerous; median gular large, triangular. Supraorbital sensory canals end back in parietals. Cleithrum arcuate, extending forwards ventrally between branchiostegal rays.

Fin rays with long proximal and short distal joints, branched distally; fulcra on all fins. Dorsal fin longer than anal, with origin above that of pelvics.

Scales rhombic and ganoine-covered; thick on anterior half of trunk, much thinner on caudal region; flank scales much deeper than long; highly ornamented by acute transverse "crimpings" in hinder halves.

Lateral line canal conspicuous, tunnelling the scales. Sensory canals tunnelling the bones through which they pass and communicating with surface by well-spaced tubuli.

Aphnelepis australis Woodward, 1895.

(Pl. III, fig. 3; text-fig. 6.)

Diagnosis. As for genus.

Holotype. An imperfect fish, lacking the cranial roof and the snout, in the Australian Museum, No. MF. 267 (Woodward,[4] Pl. III, fig. 1).

Material. The holotype and eleven other specimens in the Australian Museum numbered as follows: MF. 267-275, F. 27070, F. 39294; there are, in addition, about six useful specimens in my own collection.

Head. The head is a little longer than deep; the snout is blunt but not wide. The orbit, in diameter about one-quarter of the length of the head, is forwardly placed and situated well above the mouth. The external bones, especially those of the cranial roof and opercular series, are thick and are ornamented by coarse, short, irregular rugæ. The gape is small and is wholly in front of a line drawn through the anterior margin of the orbit.

In the greatly crushed snout, premaxillæ, a post-rostral, and nasals are determinable in specimens F. 271 and F. 272 (Pl. III, fig. 3, text-fig. 6). The premaxillæ are small, triangular, deepened only slightly at their junction. A large part of a post-rostral, bearing a cast of the sensory canal but having its inner margin destroyed, is preserved in MF. 272. Its outer margin, concave

at its junction with the lachrymal, becomes convex as it emerges dorsally into a gently convex line of junction with the nasal.

More than half the cranial roof consists of a pair of frontals the gently sinuous inner margins of which probably overlapped slightly. Their outer margins are concave above the orbits, behind which they are roughly parallel to their inner margins ; for the greater part of their width the slightly concave hinder margins are in contact with the parietals, which are roughly quadrangular, nearly as wide as long, widest where they meet. All margins are nearly straight, except the outer, where they meet the supratemporals in sinuous lines.

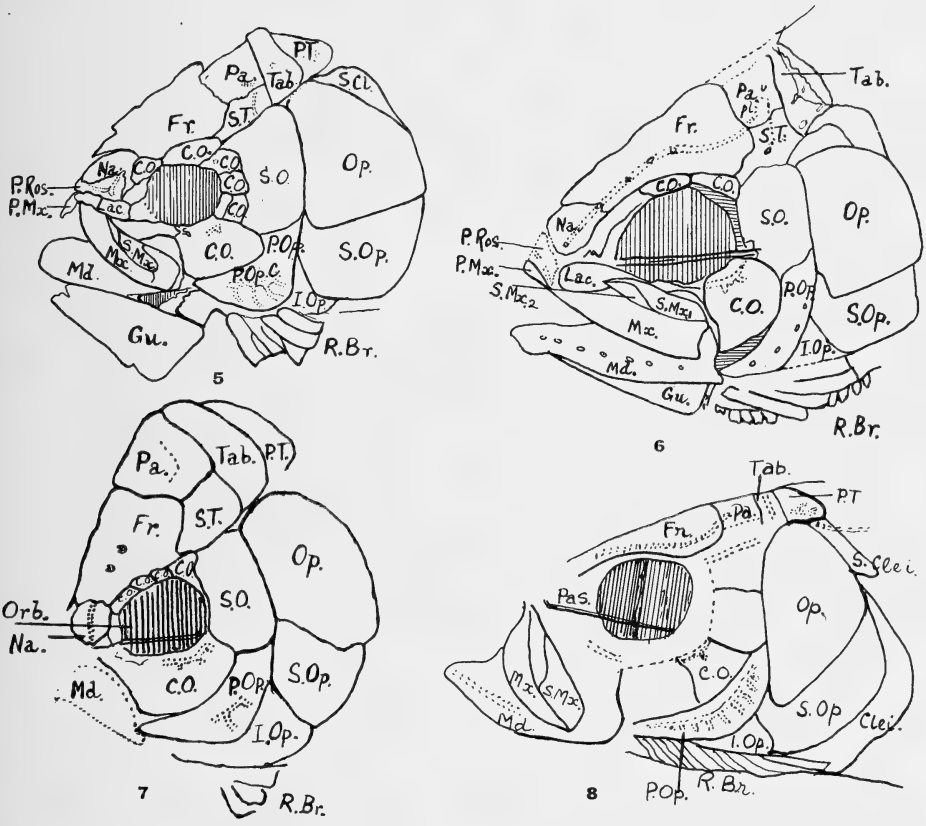

Fig. 5. *Madariscus robustus.* Head of Austr. Mus. No. MF. 256. Nat. size.

Fig. 6. *Aphnelepis australis,* head. Composite drawing based on Austr. Mus. Nos. MF. 271 and 272 (counterparts). Snout and inner margin of frontal partly restored. ×3/2.

Fig. 7. *Ætheolepis mirabilis,* head. Composite drawing based on Austr. Mus. Nos. MF. 263 and 261 (counterparts). ×3/2.

Fig. 8. *Leptolepis talbragarensis,* head. Composite drawing. ×2.

The tabulars are much wider than long, and are very short in the mid-line of the head. Post-temporals are triangular and scale-like. On each side of the head a supratemporal occupies the irregular space between the tabular, parietal, frontal, circumorbital, suborbital, and operculum.

The circumorbitals are irregular in size and shape. In front, just above the maxilla, there is a large leaf-shaped lachrymal, much longer than deep, the posterior margin of which forms a very small part of the orbital border. Above this in succession follow two bones of nearly equal size, much deeper than long,

together completing the anterior border of the orbit. Behind the orbit at the top corner lies a bone of moderate size, with a concave margin in front and a pronounced elbow behind. Probably a deep and very narrow bone extended below this to about three-quarters of the depth of the orbit, where it would meet the most conspicuous bone of the series, which in general shape suggests a valve of a shell lying diagonally over the cheek, an impression heightened by faint concentric and radial ridgings that are more pronounced towards the outer edge of the bone. The infraorbital sensory canal as it sweeps round below the orbit, and a few short radiating branches, channelled this bone deeply and are preserved as casts.

Above the latter circumorbital and occupying all the space between the operculum and the circumorbital row there is a large subovate suborbital, nearly twice as deep as long, having its upper end convex and its lower end pointed, wedged as it is between the large circumorbital and the upper end of the preoperculum.

The preoperculum, which is of moderate size, is boomerang-shaped. The operculum, large and quadrangular, is nearly twice as deep as long and has its upper margin sharply produced, its lower margin rising fairly quickly towards the rear. The subopercular, which is less than half as deep as the operculum, has curved anterior and posterior margins which meet in a blunt acute angle. Its upper anterior angle is produced to a sharply pointed process, which lies between the preoperculum and the operculum. There is a triangular interoperculum less in area than half the subopercular.

The length of the maxilla, which is a large bone, is about three times its maximum depth, which is that of its posterior margin. The upper margin is sinuous, comprising two concave segments, the hinder one shallow and extending about two-thirds of the total length of the maxilla, the anterior descending rapidly to reduce the depth of the bone in front to about one-fifth of its maximum depth. Two supra-maxillæ, the hinder about twice as large as the anterior, which it meets in a sinuous line of junction directed obliquely forward, together cover a lenticular area much longer than deep.

The mandible is very high in the coronoid region and has a very slight droop in front. The articulatory facet is clearly preserved, and angular and dentary elements may be clearly distinguished in specimens MF. 271 and MF. 272, and part of a surangular in MF. 271.

A large triangular median gular is succeeded posteriorly by six or seven short strap-like branchiostegal rays, and these by an equal number of longer rays, which gradually increase in size as they approach the opercular series.

Small, conical, sharply pointed teeth are borne by maxillæ, premaxillæ and dentaries.

The sensory canals, preserved either as open channels or as casts or rows of tubuli, are conspicuous. Pit lines appear in supratemporals, parietals, and the largest circumorbital.

Family Ætheolepidæ.

Diagnosis. Laterally compressed fishes with very deep bodies and moderate orbits placed well forward. Suspensorium forwardly inclined; gape small; external bones of skull and scales highly ornamented by tubercles. Tail almost homocercal, caudal fin not deeply forked; median fins large, paired fins small; fin rays divided into small segments, of which proximal is longest, distally branched; fulcra conspicuous.

Notochord persistent; neural and hæmal spines and also the long fin ray supports only superficially calcified.

Nasals large, irregular. Frontals long, wide behind orbits; parietals large, quadrangular; tabulars wide, short, extending behind parietals and

supratemporals ; supratemporals of moderate size, irregular, post-temporals wide, short, irregular. Circumorbital series of at least seven bones, including one large bone which extends well over cheek. One large suborbital between operculum and circumorbital ring. Operculum more than twice as large as subopercular ; interoperculum triangular, partly below subopercular, which is not greatly larger than it. Branchiostegal rays few. Preoperculum large, arcuate, extending forwards ventrally. Maxilla of moderate size, not deep ; supramaxilla small ; mandible deep anteriorly, tapering towards the back.

Cleithrum arcuate, with lower end extending forward between the branchiostegal rays.

Dorsal fin long, arising at midpoint of dorsal margin ; anal fin much smaller than dorsal.

Abdominal scales thick, rhombic, greatly deepened on flank ; caudal scales very thin, approximately cycloidal, some with pegs.

Genus **Ætheolepis** Woodward, 1895.

Diagnosis. As for family.

Genotype. *Ætheolepis mirabilis* Woodward.

Ætheolepis mirabilis (Woodward).

(Pl. III, fig. 1 ; text-fig. 7.)

Diagnosis. As for genus.

Holotype. A nearly complete fish, with poorly preserved head, No. MF. 260, in the Australian Museum.

Material. The holotype and seven other specimens in the Australian Museum, numbered MF. 260-266, F. 4110, together with three specimens in my own collection.

Head. The head is deeper than long, and its mid-line descends steeply to the small mouth. The suspensorium is forwardly inclined to such a degree that the hinder margins of the jaws meet at a point well in front of a line through the centre of the orbit. The latter, which is large, is placed centrally, and entirely in the front half of the head. The snout is probably sharply rounded. Crushed fragments only of the oral margin of the snout are preserved, but large nasals are determinable and these are deeper than wide, being widest at about their middle and narrower at top than bottom.

The frontals are large, widest just behind and somewhat contracted between the orbits. Their inner margins are not clearly revealed. Their lateral margins are concave with slight subordinate irregular concavities where bordered by three circumorbitals. Just behind these the frontals extend outwards, forming a small irregular projection separating these bones from the supratemporals Their hinder margins, which are nearly straight where they meet the parietals, are sinuous along their lines of contact with the supratemporals.

The parietals, which are larger on their inner than on their outer margins, and are about as broad as long, meet on one side or other of the mid-line of the head.

The tabulars are much wider than long, with very short common suture and they extend completely behind the parietals and supratemporals. Their hinder and front margins are both gently concave.

The supratemporals, which are smaller than the parietals, decrease greatly in depth just below the frontals and project for a short distance over that circumorbital which lies at the postero-dorsal margin of the orbit.

Seven bones of the circumorbital ring can be determined : in front of the orbit a deep, very short bone rests on an undetermined bone which was probably a lachrymal ; above this lies a long tapering bone ; next, a small ovate bone ;

then along the top margin, a circumorbital about twice as long as it is deep; at the upper corner of the back of the orbit there is a triradiate bony plate, which meets a frontal and supratemporal on its inner side, and a large suborbital behind it; behind the orbit lies a deep, narrow bone; finally below the orbit there is determinable only a very large bone, which borders the orbit for about three-quarters of the length of the latter, and extends back over the cheek to the preoperculum and suborbital; this is deeply channelled by the intra-orbital sensory canal and some of its branches.

There is one large suborbital, about twice as deep as long, which covers the area of the cheek between the circumorbital ring and the opercular series and the supratemporal.

The operculum, narrower above than below, is a little less than twice as deep as long. Its hinder margin is convex, anterior margin nearly straight, lower margin straight for the most part but sharply sinuous posteriorly. The subopercultum, which is about as deep as long, is very roughly quadrangular, being deeper behind than before, longer where it meets the operculum than below. The interoperculum is smaller than the subopercultum and is roughly triangular, projecting below the preoperculum. This latter bone is unusual in shape and extent for fishes of this order. It displays a postero-dorsal acute angle, but soon attains its maximum and nearly uniform length, bending almost at right angles just below its middle and thereafter extending forwards tapering rapidly.

In specimen No. MF. 263 (Pl. III, fig. 1; text-fig. 7) the mandible has been forced deeply into the matrix, carrying with it, to some extent, the adjoining end of the preoperculum. Unfortunately, in recovering the fossil the fracture in the rock occurred in such a manner as to destroy the anterior end of the lower jaw, the mouth, the maxilla and oral margin of the snout. In the drawing (text-fig. 7), the lowest line is the outer edge of the hollow in the matrix; there is an irregular hollow in the cast of the mandible, which is partly overhung by a small projecting fold. Posteriorly the bone is of little depth and bears a concavity at its junction with the preoperculum; anteriorly the jaw is greatly deepened. No teeth have been preserved and the species may have been toothless.

Sensory canals are displayed well only in the nasals, the largest circum-orbital, and the preoperculum. Casts of two or three of the tubuli of the supra-orbital canal occur in the frontals, and there is an angulated "pit line" in the parietals. The external bones are closely ornamented by very small tubercles.

Preliminary Note on Uarbryichthys latus, a New Jurassic Macrosemiid.

The following brief account of this new genus and species is intended merely to record its occurrence; full description must await the return from London of specimens now in the care of Professor D. M. S. Watson.

Diagnosis. Small macrosemiids resembling *Histionotus* but having head more depressed. Dorsal fin arising near back of head and extending to tail, other fins small. Pelvics placed halfway between anal and pectorals. Fin rays with long proximal joints but distally divided into small segments and branching several times. Pectorals with scaleless lobe and at least five elongated basals expanded distally; fleshy upper lobe of tail slightly produced. Scales rhombic, ganoine-covered; principal flank scales only slightly deeper than long; scales elaborately ornamented with short, irregular, transverse rugæ.

Genotype. Uarbryichthys latus (the only species).

Material. (1) Type specimen, in writer's collection, a nearly complete fish, with trunk and part of head in counterpart (the head at present in care of Professor D. M. S. Watson).

(2) A less complete specimen in the Mining Museum, Sydney (now in London).

(3) Several fragments showing scale and fin structure (in writer's collection).

Holotype. The length of the trunk from the back of the head to the base of the tail is 135 mm.; the maximum depth, which occurs just behind the lobe of the pectoral fins, is about 62 mm.; the depth of the base of the tail is 18 mm.

In the long dorsal fin there are more than forty rays, which have a markedly long proximal segment, thereafter are divided into very small segments and branch several times. At the origin of the fin about eight short rays, gradually increasing in length, precede a few long stout rays, which are placed fairly closely together and are followed by stout well-spaced rays of decreasing length. All the fins are incomplete, but it is quite clear that the pectorals, which comprise more than fourteen rays, are comparatively large, but that the pelvics, which probably included ten rays, the anal, of which only four rays are preserved, and the caudal were quite small.

Leptolepis.

(Text-fig. 8.)

These fishes have been preserved in shoals; specimens are literally innumerable. The heads are all flattened and only external structures can be determined, as shown in text-fig. 8, which is included in this paper merely for record purposes.

Previously three species have been assigned to the genus from this locality, but in view of the uniformity of the structure of the head the writer is convinced that only one species, *Leptolepis talbragarensis*, need be recognised, the specific differences previously relied on being due to individual peculiarities or mode of preservation or differences in maturity.

List of the Farr's Hill Fish Fauna.

Crossopterygii.

Cœlacanthidæ .. .. Genus non det.

Palæopterygii.

Palæoniscidæ .. .. *Coccolepis australis* Woodward.

Neopterygii.

Order Holostei.

Macrosemiidæ .. .. *Uarbryichthys latus* gen. et sp. nov.

Sub-Order Cenogenoidei.

Ætheolepidæ .. .. *Ætheolepis mirabilis* Woodward.
Aphnelepidæ .. .. *Aphnelepis australis* Woodward.
Archæomænidæ .. .. *Archæomæne tenuis* Woodward.
Madariscus robustus gen. nov.

Order Teleostei.

Leptolepidæ .. .. *Leptolepis talbragarensis* Woodward.

Summary.

This paper deals chiefly with the external structure of the heads of *Archæomæne tenuis*, *Madariscus robustus*, *Aphnelepis australis* and *Ætheolepis mirabilis*.

These fishes are presented here as comprising a small group, the Cenogenoidei, having a characteristic cheek, squamation, and endoskeleton—a group which developed in isolated fresh waters, probably from one or more species of the family Pholidophoridæ, evolving convergently with *Leptolepis*.

A drawing of the head of, and a short note on, *Leptolepis* is included for the purpose of recording the opinion of the author that there is but one species here, namely *L. talbragarensis*.

There is a preliminary note on a new Jurassic Macrosemiid, *Uarbryichthys latus*, the generic name being derived from the locality, Uarbry Road.

Acknowledgments.

Photographs of the casts in dental wax reproduced in Plate III, figs. 1, 2, 3 were supplied by Professor D. M. S. Watson, to whose help and encouragement the author owes much. Figs. 1 and 2, Plate II, and fig. 4, Plate III, are from photographs by the Reverend Frank Cash. The restoration of *Archæomœne tenuis* (text-fig. 4) is by Mr. G. P. Whitley, Australian Museum.

References.

(1) Dulhunty, J. A.: Notes on the Stratigraphy and Physiography of the Talbragar "Fish-Bed" Area, This Journal, 1937, *71*, 350-356.

(2) Goodrich, E. S.: Vertebrata Craniata, p. 37 (in Ray Lankester, "A Treatise on Zoology", Part IX, 1909).

(3) Westoll, T. S.: On the Cheek Bones in Teleostome Fishes, *Journ. of Anatomy*, Cambridge, 1937, *71*, 362-382.

(4) Woodward, A. S.: The Fossil Fishes of the Talbragar Beds (Jurassic), *Memoir Geol. Surv. N. S. Wales*, Palæont., No. 9, 1895.

Explanation of Plates.

Plate II.

Fig. 1. *Archæomœne tenuis*, Austr. Mus. No. F. 39292. ×8/13, approx.

Fig. 2. *Archæomœne tenuis*, Austr. Mus. No. F. 39293. Showing head, position of fins, and squamation. ×10/3.

Plate III.

Fig. 1. *Ætheolepis mirabilis*, Austr. Mus. No. MF. 263. Cast of head (reversed). Compare text-fig. 7. ×4/3, approx.

Fig. 2. *Madariscus robustus*, Austr. Mus. No. MF. 256. Cast of head (reversed). Compare text-fig. 5. Nat. size, approx.

Fig. 3. *Aphnelepis australis*, Austr. Mus. No. MF. 271. Cast of head (reversed). Compare text-fig. 6. ×4/3, approx.

Fig. 4. *Aphnelepis australis*, Austr. Mus. No. F. 39294. Head, especially cranial roof and snout. ×3, approx.

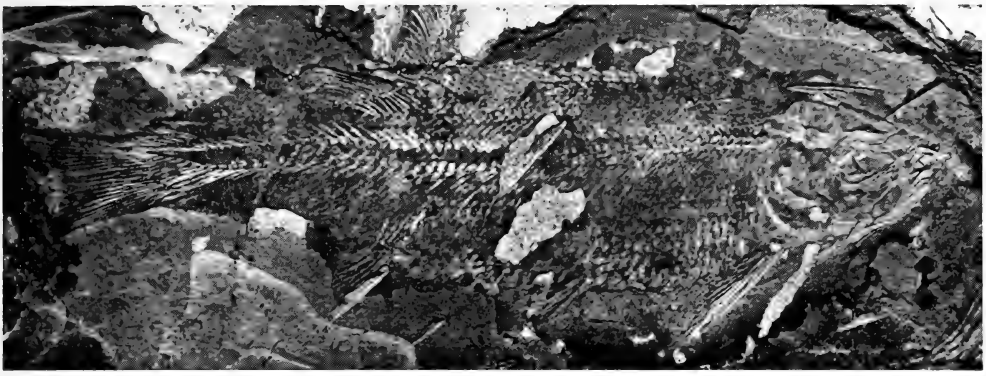

Fig. 1.

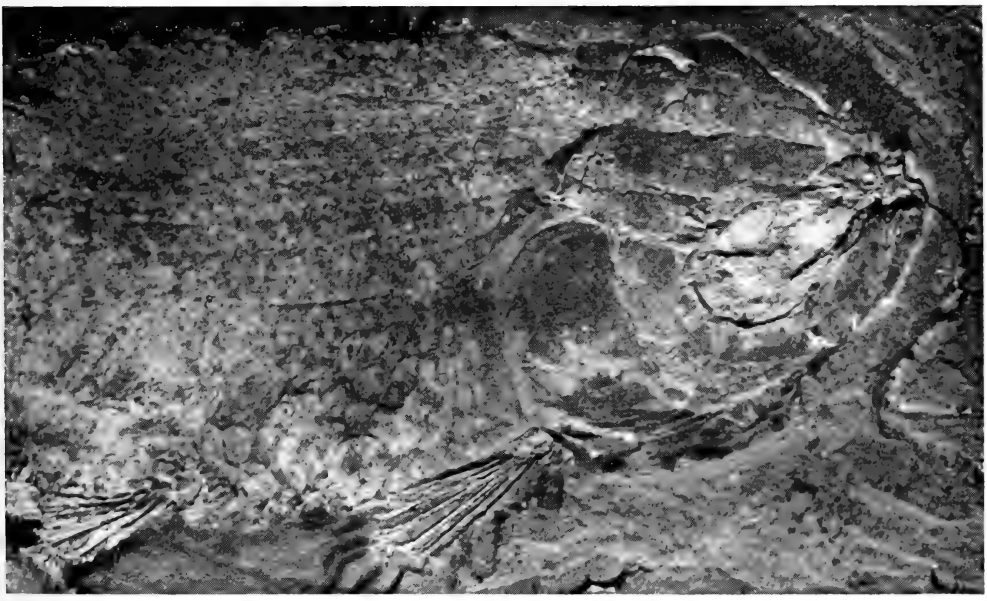

Fig. 2.

1

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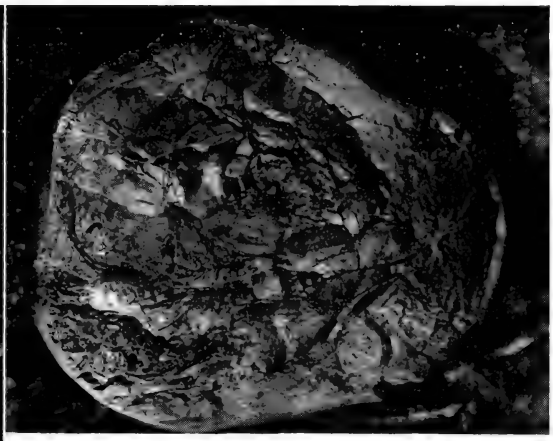

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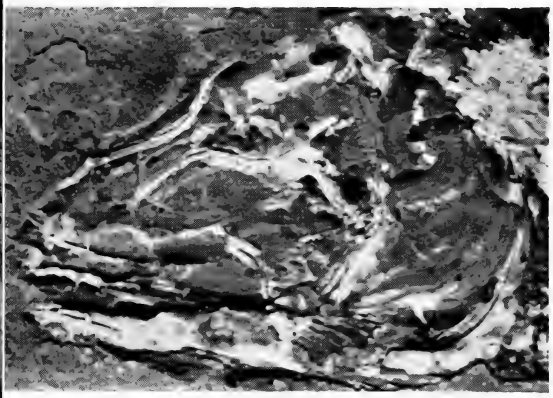

REMARKS ON GOODNESS OF FIT OF HYPOTHESES AND ON PEARSON'S χ^2 TEST.

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(*Manuscript received, June 4, 1941. Read, July 2, 1941.*)

I. Simple Tests of Sets of Standard Normal Variates.

In a recent paper,[1] cited herein as E.P., it was noted that if the hypothesis leads to consideration of values of n statistically independent standard or "reduced" normal variates $x_1, x_2, \ldots . x_n$ (each with mean 0 and standard deviation 1), it is not sufficient to consider their χ^2 in order to decide whether the observed values form a rare set; that we must first examine the signs of the observed values, and if the distribution of signs is not so unequal, or so systematic, as to disturb our confidence in the fitness of the hypothesis, we may consider their χ_n^2, but must then also consider the value of the Beta variate $b\left(\frac{1}{2}, \frac{n-1}{2}\right) = \chi_1^2/\chi_n^2$, χ_1^2 being the square of any chosen one of the observed values, or the value of the corresponding t_{n-1} variate $x_1 \Big/ \sqrt{\left\{\frac{1}{n-1}(\chi_n^2 - \chi_1^2)\right\}}$, and also the values of the remaining Beta variates, or of the corresponding t variates, there being in all $(n-1)$ Beta or t variates for examination as well as the χ_n^2 variate.[2]

This amounts to saying that if the set is to be regarded as not rare, then not only must the sum of the squares of the observed values not have a rare value, but also the ratio of the square of one to the sum of the squares of all must not have a rare value (allowing for permutations), and so on.

It was also noted that in this case of *standard* normal variates the observed values may be more directly tested, and an example was given to show that the frequency with which sets of 11 standard normal variates contain one or more members exceeding 2·8 is about 0·05.[3] As it will presently be shown that Pearson's χ^2 test of goodness of fit is merely the abovementioned χ^2 test of a determinable set of statistically independent standard normal variates, and is therefore imperfect, some further examples are now given to illustrate this direct method.

(1) The set of ten standard normal variates 2·3, 2·2, 0·2, 0·1, −0·3, −0·4, −0·5, −0·6, −1·0, −1·1 has a satisfactory distribution of signs and shows $\chi_{10}^2 = 13 \cdot 34$.

As the frequency with which this value is exceeded is about 0·2, this set of ten, when judged in the usual way by the χ^2 test, is not of an uncommon kind. There are, however, two members certainly greater than 2·15, supposing that the values are forced to one place of decimals and that closer values are not

[1] D. T. Sawkins, Elementary Presentation of the Frequency Distributions of Certain Statistical Populations Associated with the Normal Population, *Jour. Roy. Soc. N. S. Wales*, 1940, *74*, 209–239. [E.P.]

[2] E.P., pp. 220–224.

[3] E.P., p. 220.

available. By the normal table the frequency with which a single s.n.v. exceeds 2·15 in absolute value is 0·0318. Hence the f. of sets of 10 which contain two or more members numerically greater than 2·15 is the sum of all terms but the first two of the expansion of $(0\cdot9682+0\cdot0318)^{10}$, which works out to about 0·04. So in spite of the χ^2 test, this set is of a rare sort.

(2) The set 2·0, 1·8, 0·3, 0·2, 0·1, −0·4, −0·6, −1·0, −1·1, −1·8 also passes the sign test (provided that the order has no significance, as it might easily have in a cell test), and also passes the χ^2 test as $\chi_{10}^2=13\cdot35$. But three members exceed 1·75 numerically. The f. with which a single s.n.v. exceeds 1·75 in absolute value is 0·0805. Hence the proportion of sets of 10 which contain three or more such members is the sum of all but the first three terms of the binomial $(0\cdot9195+0\cdot0805)^{10}$, which works out to about 0·04. So this set also is of a rare kind.

II. The χ^2 Distribution for Cell Frequencies.

The proofs of this distribution given by K. Pearson in 1900[4] and R. A. Fisher in 1922[5] begin with the assumption that for each cell the mean or "expected" number is so large that the number in each cell is normally distributed. In a text book published in 1939, A. C. Aitken states that "the derivation of the χ^2 distribution involves the general multivariate normal correlation function", and sketches the outlines of a proof which proceeds at once to the limit towards which the compound frequency density tends as the number of trials N increases, provided that the mean number for no cell fails to increase ("provided no p is of order $\frac{1}{N}$"), and so, in effect, makes the same assumption as Pearson and Fisher.[6] The proof given by J. V. Uspensky in a text book published in 1937 emphasises that the χ^2 cell theorem is a limit theorem, i.e. that this χ^2 distribution is the limit towards which an actual distribution tends, provided that the mean number for *every* cell increases,[7] and observes that "*the lack of information as to the error incurred*" by using the limiting form when the mean numbers for one or more cells are not large "*renders the application of this χ^2 test devised by Pearson somewhat dubious.*"[8]

It is not the purpose of this short paper to discuss such errors at length, but to show that this χ^2 test is an imperfect and sometimes misleading test even when the mean numbers for all the cells are so large that these errors are quite negligible. However, as the classical approach to the problem suggests one way of assessing the errors of approximation and leads directly to a derivation of the limiting form, an outline of this solution is presented.[9]

If p_r is the frequency with which an individual enters the rth of n cells, then for a set of N individuals whose distributions are statistically independent, the frequency with which there are $\alpha_1, \alpha_2, \ldots \alpha_n$ individuals in the n cells respectively is

$$F=p_1^{\alpha_1}\, p_2^{\alpha_2} \ldots p_n^{\alpha_n}\, \frac{N!}{\alpha_1!\,\alpha_2!\ldots\alpha_n!}, \text{ where } S(p)=1,\ S(\alpha)=N.$$

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[4] K. Pearson, "On the Criterion....", *Phil. Mag.*, 1, Series 5, 1900, *50*, 157–175.

[5] R. A. Fisher, "On the Interpretation of χ^2....", *Jour. Roy. Stat. Soc.*, 1922, *85*, 87–94.

[6] A. C. Aitken, "Statistical Mathematics", Oliver and Boyd, Edinburgh and London, 1939, p. 101.

[7] J. V. Uspensky, "Introduction to Mathematical Probability", McGraw-Hill Book Co., New York and London, 1937, p. 325, line 13.

[8] *Idem*, p. 327.

[9] See Borel and Lagrange, Traité du Calcul des Probabilités et ses Applications, Paris, 1925, Tome I, Fasc. I, pp. 33–36, and Bowley, Elements of Statistics, 6th ed., London, 1937, p. 454.

Using Stirling's formula, $\log_e k! = (k+\frac{1}{2}) \log k - k + \log \sqrt{2\pi} + \varepsilon_k$ where $\varepsilon_k = \frac{1}{12k}$ approximately, we have

$$\begin{aligned}\log_e F = {} & \alpha_1 \log p_1 + \alpha_2 \log p_2 + \ldots . \\ & + (N+\tfrac{1}{2}) \log N - N + \log \sqrt{2\pi} + \frac{1}{12N} \\ & - (\alpha_1+\tfrac{1}{2}) \log \alpha_1 + \alpha_1 - \log \sqrt{2\pi} - \frac{1}{12\alpha_1} \\ & - (\alpha_2+\tfrac{1}{2}) \log \alpha_2 + \alpha_2 - \log \sqrt{2\pi} - \frac{1}{12\alpha_2} \\ & \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot\end{aligned}$$

Hence, noting that $N = \alpha_1 + \alpha_2 + \ldots . + \alpha_n$,

$$\log F = -\sum_{r=1}^{n} \left\{ (\alpha_r + \tfrac{1}{2}) \log \frac{\alpha_r}{N p_r} \right\} - \tfrac{1}{2} \log (p_1 p_2 \ldots . p_n) - \frac{n-1}{2} \log (2\pi N) + \delta,$$

$$\text{where } \delta = \frac{1}{12} \left\{ \frac{1}{N} - S\left(\frac{1}{\alpha_r}\right) \right\} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (1)$$

Writing m_r for $N p_r$, which is the mean number of individuals for the rth cell, and putting $\frac{\alpha_r}{N p_r} = 1 + \frac{x_r}{m_r}$, so that x_r is the deviation from that mean number, we have

$$\sum_{1}^{n} (\alpha_r + \tfrac{1}{2}) \log \frac{\alpha_r}{N p_r} = \sum_{1}^{n} (m_r + x_r + \tfrac{1}{2}) \left(\frac{x_r}{m_r} - \frac{x_r^2}{2m_r^2} + \frac{x_r^3}{3m_r^3} - \ldots . \right).$$

Since $\sum_{r=1}^{n} x_r = 0$, this may be arranged in the form

$$\tfrac{1}{2} \sum_{r=1}^{n} \left(\frac{x_r^2}{m_r} + \frac{x_r}{m_r} - \frac{x_r^3}{3m_r^2} - \frac{x_r^2}{2m_r^2} + \frac{x_r^4}{6m_r^3} + \ldots . \right) \quad \ldots \ldots \ldots \quad (2)$$

When x_r is of order $\sqrt{m_r}$ the 1st term in the bracket is of order 1, the 2nd and 3rd are of order $1/\sqrt{m_r}$, the 4th and 5th are of order $1/m_r$, and so on. If all the m_r are large enough to permit terms of order $1/m$ to be neglected, we may omit the 4th, 5th and higher terms in the bracket, also the δ in (1).

The correction to $\frac{x^2}{m}$ due to the 2nd and 3rd terms combined is then $\frac{x}{m}\left(1 - \frac{x^2}{3m}\right)$. Considering positive x, this increases until $x = \sqrt{m}$. Then $\frac{x^2}{m} = 1$, and the correction is $\frac{2}{3\sqrt{m}}$, which when $m = 10$ is about $0 \cdot 2$, and when $m = 50$ is about $0 \cdot 1$. When $x = \sqrt{3m}$ the correction vanishes (as does also the combination of the 4th and 5th terms). When $x = 2\sqrt{m}$, $\frac{x^2}{m} = 4$ and the correction is $-\frac{2}{3\sqrt{m}}$. Although $\sum_{1}^{n} \left\{ \frac{x}{m}\left(1 - \frac{x^2}{3m}\right) \right\}$ is a mixture of positive and negative elements since $\sum_{1}^{n} (x) = 0$, it can take appreciable values in ordinary practice, as, for example, in the distribution of 1,000 stellar observations quoted below at p. 90.

Hence from (1) and (2) the frequency is approximately

$$F = \frac{1}{\sqrt{(p_1 p_2 \ldots . p_n)(2\pi N)^{n-1}}} \exp \left\{ -\tfrac{1}{2} \sum_{r=1}^{n} \left(\frac{x_r^2}{m_r} \right) - \tfrac{1}{2} S\left(\frac{x_s}{m_s} - \frac{x_s^3}{3m_s^2} \right) \right\}$$

$$\ldots \ldots \ldots \ldots \ldots \ldots \quad (3)$$

GG—July 2, 1941.

where the second summation includes only those cells for which the mean number, while large enough to permit rejection of $O(1/m)$, is not large enough to allow rejection of $O(1/\sqrt{m})$.

As the coefficient of this exponential is $\sqrt{N}/\sqrt{(m_1 m_2 \ldots m_n)}(2\pi)^{\frac{1}{2}(n-1)}$, the frequency with which any particular set $(\alpha_1, \alpha_2, \ldots \alpha_n)$ occurs is extremely small. If, however, we calculate the total frequency of the $(\alpha'_1-\alpha_1+1)(\alpha'_2-\alpha_2+1)\ldots(\alpha'_{n-1}-\alpha_{n-1}+1)$ sets in which the integral numbers in $(n-1)$ of the cells range from α_1 to α'_1, α_2 to $\alpha'_2, \ldots \alpha_{n-1}$ to α'_{n-1} inclusive in each case (the number in the remaining cell being then determined by the relation $\overset{n}{\underset{r=1}{S}}(\alpha_r)=N$, which holds for every set), we may have a tangible total frequency provided that each factor $(\alpha'_r-\alpha_r+1)$ is of order $\sqrt{m_r}$. The summation of frequencies may be performed by successive applications of the Euler-Maclaurin theorem in the form

$$F(x)+F(x+1)+\ldots+F(x+h)$$
$$=\int_{x-\frac{1}{2}}^{x+h+\frac{1}{2}} F(t)dt-\frac{1}{24}\{F'(x+h+\tfrac{1}{2})-F'(x-\tfrac{1}{2})\}+\ldots$$

the next term on the right (involving the 3rd derivates) having a very small coefficient, $\frac{1}{823}$ nearly.[10]

For a first application we have $\frac{\partial F}{\partial x_1}=\left(\frac{x_n}{m_n}-\frac{x_1}{m_1}\right)F$ nearly. We may choose as the nth cell one whose m is large enough to allow rejection of $O(1/\sqrt{m_n})$. So when each x_r is $O(\sqrt{m_r})$, $\frac{\partial F}{\partial x_1}$ is of order $F/\sqrt{m_1}$. Even when m_1 is as small as 10, and the summation is from $\alpha=6$ to $\alpha'=14$, this correction, in view of the coefficient $\frac{1}{24}$, is of the order of $\frac{1}{24}$ of the smallest of the nine terms included in the summation. Hence the total frequency is approximately

$$\frac{(2\pi)^{-\frac{1}{2}(n-1)}}{\sqrt{(m_1 m_2\ldots m_{n-1})}\sqrt{p_n}}\int_{\alpha_1-m_1-\frac{1}{2}}^{\alpha'_1-m_1+\frac{1}{2}}\ldots\ldots\int_{\alpha_{n-1}-m_{n-1}-\frac{1}{2}}^{\alpha'_{n-1}-m_{n-1}+\frac{1}{2}}$$
$$\exp\left\{-\tfrac{1}{2}\overset{n}{\underset{r=1}{S}}\left(\frac{x_r^2}{m_r}\right)-\tfrac{1}{2}S\left(\frac{x_s}{m_s}-\frac{x_s^3}{3m_s^2}\right)\right\}dx_1\ldots dx_{n-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Putting $x_r/\sqrt{m_r}=t_r$, this becomes

$$\frac{(2\pi)^{-\frac{1}{2}(n-1)}}{\sqrt{p_n}}\int\ldots\int\exp\left[-\tfrac{1}{2}\overset{n}{\underset{r=1}{S}}(t_r^2)-\tfrac{1}{2}S\{(t_s-\tfrac{1}{3}t_s^3)/\sqrt{m_s}\}\right]dt_1\ldots dt_{n-1}$$
$$\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

the field of integration being from $(\alpha_r-m_r-\frac{1}{2})/\sqrt{m_r}$ to $(\alpha'_r-m_r+\frac{1}{2})/\sqrt{m_r}$, $\{r=1\ldots(n-1)\}$.

Now if $\alpha<m<\alpha'$, and $(\alpha+\alpha')$ forms the nearest integer to $2m$, then $|\alpha-m-\frac{1}{2}|$ and $(\alpha'-m+\frac{1}{2})$ do not differ by more than $\frac{1}{2}$, and even in the case of a cell with a small mean number such as 10, $\mp(\alpha'-\alpha+1)/2\sqrt{m}$ may be used as the limits of integration, for this displaces both limits in the same sense by $1/4\sqrt{m}$ at most.

[10] L. M. Milne-Thompson, Calculus of Finite Differences, Macmillan and Co., London, 1933, p. 190.

In the case of any cell which contributes to the second summation in the exponent, the relevant part of the integral is

$$\int_{-t_0}^{t_0} \exp\left[-\tfrac{1}{2}\left\{t^2+t_n{}^2+\frac{1}{\sqrt{m}}(t-\tfrac{1}{3}t^3)+\frac{1}{\sqrt{m_n}}(t_n-\tfrac{1}{3}t_n{}^3)\right\}\right]dt$$

$$=\int_{-t_0}^{t_0} e^{-\frac{1}{2}(t^2+t_n{}^2)}\left\{1-\frac{1}{2\sqrt{m}}(t-\tfrac{1}{3}t^3)-\frac{1}{2\sqrt{m_n}}(t_n-\tfrac{1}{3}t_n{}^3)\right\}dt$$

approximately. Recalling that the nth cell has been chosen so that $O(1/\sqrt{m_n})$ may be neglected, this integral becomes

$$\int_{-t_0}^{t_0} e^{-\frac{1}{2}(t^2+t_n{}^2)}\,dt+\left|\frac{1}{6\sqrt{m}}(1-t^2)e^{-\frac{1}{2}(t^2+t_n{}^2)}\right|_{-t_0}^{t_0},$$

and referring to equation (7) below, the second term

$$=\frac{1}{6\sqrt{m}}(1-t_0{}^2)e^{-\frac{1}{2}t_0{}^2}\left|e^{-\frac{1}{2}t_n{}^2}\right|_{-t_0}^{t_0},$$

or approximately

$$\frac{1}{3\sqrt{m_n}}(t_0-t_0{}^3)e^{-\frac{1}{2}t_0{}^2}\ .\ t_ne^{-\frac{1}{2}t_n{}^2},\ \text{i.e.}<\frac{1}{3\sqrt{m_n}}\ \text{numerically.}$$

Hence the total frequency is approximately

$$\frac{(2\pi)^{-\frac{1}{2}(n-1)}}{\sqrt{p_n}}\int\cdots\int e^{-\frac{1}{2}\overset{n}{\underset{r=1}{S}}t_r{}^2}\,dt_1\ldots dt_{n-1}\quad\ldots\ldots\quad(6)$$

with limits of integration as shown above.

Since $\overset{n}{\underset{1}{S}}(x)=0$ we have $t_1\sqrt{m_1}+t_2\sqrt{m_2}+\ldots+t_n\sqrt{m_n}=0$ ..... (7)

Take $(n-1)$ new variables, viz.

$$v_0=\frac{-1}{\sqrt{m_1+m_2+\ldots+m_{n-1}}}(t_1\sqrt{m_1}+t_2\sqrt{m_2}+\ldots+t_{n-1}\sqrt{m_{n-1}})$$

.....(8)

and $v_1, v_2, \ldots v_{n-2}$ forming an orthogonal set so that $\overset{n-2}{\underset{0}{S}}(v^2)=\overset{n-1}{\underset{1}{S}}(t^2)$.[11]

From (7) and (8), $v_0\sqrt{N-m_n}=t_n\sqrt{m_n}$, $t_n{}^2=\left(\frac{1}{p_n}-1\right)v_0{}^2$.

Hence $\overset{n}{\underset{1}{S}}(t^2)=\overset{n-2}{\underset{0}{S}}(v^2)+\left(\frac{1}{p_n}-1\right)v_0{}^2=\frac{v_0{}^2}{p_n}+\overset{n-2}{\underset{1}{S}}(v^2)$ ..... (9)

The jacobian is ±1. Hence the integral (6) becomes

$$\int\frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}v_0{}^2/p_n}\,d(v_0/\sqrt{p_n})\ .\ \int\frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}v_1{}^2}dv_1\ldots\int\frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}v_{n-2}{}^2}dv_{n-2},$$

with appropriate limits corresponding to those of (6). Therefore $v_0/\sqrt{p_n}$, $v_1, \ldots v_{n-2}$ are statistically independent standard normal variates.

We may examine these $(n-1)$ variates by various methods, including the two methods referred to at p. 85.

First we may say that the sum of their squares, which by (9) is $\overset{n}{\underset{1}{S}}\left(\frac{x^2}{m}\right)$, is a $\chi_{n-1}{}^2$, i.e. that $\frac{1}{2}\overset{n}{\underset{1}{S}}\left(\frac{x^2}{m}\right)$ is a Gamma variate $c\left(\frac{n-1}{2}\right)$ whose c.f. from a

[11] E.P., pp. 215, 230.

particular value u to ∞ is $\int_u^\infty \frac{1}{\Gamma\left(\frac{n-1}{2}\right)} e^{-u} u^{\frac{n-1}{2}-1} du$. By putting $\frac{1}{2}\chi^2$ for u, this integral takes the form in which it was originally written in 1900 by Karl Pearson.

But, as pointed out at p. 85, there are also $(n-2)$ Beta variates (or corresponding t variates) to be examined before we can be satisfied with the "goodness of fit" of the hypothesis which may be indicated by the χ^2 test alone.

Secondly, we may proceed by the more direct method illustrated at pp. 85, 86, and in order to do so it is necessary to specify all members of the orthogonal set.

As $$v_0=\frac{-1}{\sqrt{N-m_n}}(t_1\sqrt{m_1}+t_2\sqrt{m_2}+\ldots+t_{n-1}\sqrt{m_{n-1}})$$

we may choose $v_r=-k_r(c_r t_r\sqrt{m_r}+\ldots+t_{n-1}\sqrt{m_{n-1}})$

where $0=c_r m_r+m_{r+1}+\ldots+m_{n-1}$

and $k_r=(c_r^2 m_r+m_{r+1}+\ldots+m_{n-1})^{-\frac{1}{2}}$.[12]

Now replacing t_r by $x_r/\sqrt{m_r}$ and briefly writing $S(x)$ for $\overset{n-1}{\underset{s=r+1}{S}}(x_s)$, we have

$$v_r=\left\{\frac{x_r}{m_r}-\frac{S(x)}{S(m)}\right\}\Big/\sqrt{\frac{1}{m_r}+\frac{1}{S(m)}}$$

$$=\left\{\frac{x_r}{\sqrt{m_r}}-\frac{\sqrt{m_r}\,S(x)}{S(m)}\right\}\Big/\sqrt{1+\frac{m_r}{S(m)}} \quad \ldots\ldots\ldots\ldots (10)$$

For the first of the standard normal variates we have from (7) and (8)

$$\frac{v_0}{\sqrt{p_n}}=\frac{t_n\sqrt{m_n}}{\sqrt{p_n(N-m_n)}}=\frac{x_n}{\sqrt{Np_nq_n}} \text{ where } q_n=1-p_n \quad \ldots\ldots\ldots (11)$$

Already m_n has been referred to one of the larger cells and we may now refer m_1, m_2, ... to those cells which show the more questionable values of $x/\sqrt{m}$. From (10) it appears that when there are many cells, as in the following example, v_1 does not differ greatly from $x_1/\sqrt{m_1}$ as $m_1/\overset{n-1}{\underset{s=2}{S}}(m_s)$ is usually small; likewise for further early members of the orthogonal set.

The following table (p. 91) is based on results of 1,000 observations made at Greenwich of the Right Ascension of Polaris, tabulated in Whitaker and Robinson's Calculus of Observations, 1924, p. 174. The first three cells, also the last two, as there given are combined, so that for no cell is m less than 25. As the parameters of the normal curve fitted to the data, viz. mean 0·06, standard deviation 1·2, are evidently not derived from these particular observations, the number of statistically independent standard normal variates arising from the fitting is one less than the number of cells considered. The table shows the usual calculation of $S\left(\frac{x^2}{m}\right)$, also the values of $\frac{x}{m}\left(1-\frac{x^2}{3m}\right)$, and of the earlier members of the orthogonal set.

From the 5th column the value of χ_{10}^2 as usually computed is 14·1. As the frequency of larger values is about 0·17, the observed value is regarded by the usual reasoning as not lying at a "high level of significance". (It will be seen in §III that this reasoning is not valid, and that the observed value really lies at an even lower level of significance than thus appears.)

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[12] E.P., p. 230.

(1) Chosen Order of Cell.	(2) α	(3) m	(4) x	(5) $\frac{x^2}{m}$	(6) $\frac{x}{m}\left(1-\frac{x^2}{3m}\right)$	(7) x'	(8) $\frac{x'}{\sqrt{m}}$	(9) v
	39	34·0	5·0	0·74	0·1	5·5	0·94	
	43	45·3	−2·3	0·12		−3·0	−0·45	
	74	81·8	−7·8	0·75	−0·1	−8·5	−0·94	
	126	121·5	4·5	0·17		5·0	0·46	
	150	153·8	−3·8	0·09		−4·5	−0·36	
11	168	166·2	1·8	0·02		*2·5*	0·19	0·22
	148	147·6	0·4	0·00		1·0	0·08	
2	129	111·9	17·1	2·62		17·5	1·65	1·58
	78	72·4	5·6	0·43	0·1	6·0	0·70	
	33	38·4	−5·4	0·76	−0·1	−6·0	−0·97	
1	12	27·1	−15·1	8·40	1·0	−15·5	−2·98	−3·01
	1000	1000·0	0·0	14·1	1·0	0·0	....	

In column (7) the value of x', the mean deviation used in deriving expression (6), is found by increasing the observed deviation numerically by $\frac{1}{2}$ and forcing this result to the nearest half unit, except in the case of the largest cell, chosen as No. 11, which is adjusted so that $\overset{11}{\underset{1}{S}}(x')=0$. In column (9) three of the ten independent standard normal variates are shown, these being more than enough to show that the inference from the value of χ_{10}^2 is quite misleading.

The value of v_0, derived from cell 11, is $\frac{2\cdot5}{\sqrt{(166\cdot2\times0\cdot8328)}}=0\cdot22$. From equation (10), $v_1=\left\{\frac{-15\cdot5}{\sqrt{27\cdot1}}-\frac{\sqrt{27\cdot1}(-2\cdot5+15\cdot5)}{1000-166\cdot2-27\cdot1}\right\}\left(1+\frac{27\cdot1}{806\cdot7}\right)^{-\frac{1}{2}}=-3\cdot01$, and so does not greatly differ from $x'_1/\sqrt{m_1}$, as anticipated.

Now the frequency with which a set of ten statistically independent s.n.v. contains one or more members as large numerically as 3·01 is $1-(0\cdot9974)^{10}=1-(1-0\cdot0026)^{10}=0\cdot026$ approx. So in spite of the χ^2 test the normal curve with the above parameters fits this set of observations badly.

The argument of the last paragraph will be made quite conclusive if we consider for the suspected cell, viz. cell 1 in the chosen order, the range 13 to 41 and so exclude the observed number 12. The corresponding value of v_1 is then −2·89 instead of −3·01. To include the observed number 12 we must increase the range of v_1 beyond $\mp2\cdot89$; the frequency with which one or more among a set of ten s.n.v. take values beyond this range is 0·04. Hence the fit is bad.

A case when there are several cell numbers whose combined presence makes the fit suspect is as shown in the table on p. 92.

Here in cells 1, 2, 3 (chosen order) the observed number is brought nearer by one to the mean number for the cell; x' and v are computed as above and $\frac{x^2}{m}$ as usually. As $S\left(\frac{x^2}{m}\right)=13\cdot2$, a value of χ_{10}^2 which is exceeded with the frequency 0·2, the fit is held by the usual reasoning to be tolerably good.

On the other hand, there are three among ten independent s.n.v. numerically exceeding 1·75, an event with the frequency 0·04. So the fit is bad.

Chosen Order.	Observed Number.	Considered Number.	m	x'	$\frac{x'}{\sqrt{m}}$	v	$\frac{x^2}{m}$
	39	39	34·0	5·5	0·94		0·74
	43	43	45·3	−3·0	−0·45		0·12
3	65	*66*	81·8	−16·5	−1·82	−1·78	3·45
	126	126	121·5	5·0	0·45		0·17
	150	150	153·8	−4·5	−0·36		0·09
11	168	167	166·2	1·5	0·12	0·13	0·02
	149	149	147·6	2·0	0·16		0·01
2	132	*131*	111·9	19·5	1·84	1·87	3·62
	78	78	72·4	6·0	0·71		0·43
	33	33	38·4	−6·0	−0·97		0·76
1	17	*18*	27·1	−9·5	−1·82	−1·84	3·76
Total ..	1000	1000	1000·0	0·0			13·2

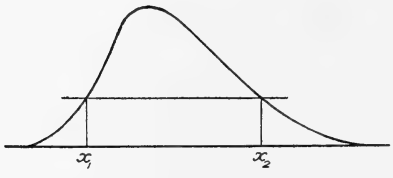
In a large number of cases the goodness of fit can apparently be well judged by inspection of the column $x'/\sqrt{m}$ without computing v, or $S\left(\frac{x^2}{m}\right)$.

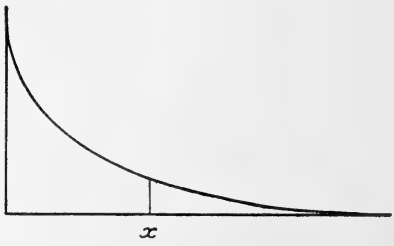
III. Confidence Ranges.

Exception was taken in §II to the practice of considering a single tail of a skew distribution such as that of χ_{10}^2 in estimating the "significance" of an observed value. It is proposed now to show that this practice is fallacious.

A confidence range is defined as a range of values of the variate such that every possible value of the variate within this range has a greater frequency than every possible value without this range.

If the frequency curve is drawn for a continuous distribution fading on both sides of its mode, any parallel to the variate axis cutting the curve gives two values of the variate x_1, x_2 at which the frequency densities are equal, and the range of values from x_1 to x_2 is a confidence range, whether the curve is symmetrical or not.





In a positive J-shaped distribution the range of values up to any value x is a confidence range.

Let us first consider the estimation of significance in the case of a discrete variate. Suppose that a variate used to form a judgment of the validity of an hypothesis which may be true or false, takes only integral values (x) with

frequencies (f) as shown in the adjacent table. Successive confidence ranges are 8 (single value), 8 and 9, 8 to 10, 8 to 11, 7 to 12, 7 to 13, etc. Suppose a single experiment or trial leads to the value 8. Only one value can occur. Whatever the frequency of the value 8, the governing consideration is that it has a greater frequency than any other value. Hence our confidence in the hypothesis is not at all disturbed. Suppose the experiment gives the value 7. Although this value occurs in the long run in only 8 per cent. of such experiments, values which occur more frequently, viz. those in the confidence range 8 to 11, occur in only 75 per cent. of trials. This confidence range then is not very exhaustive, for values outside it occur in as many as 25 per cent. of trials. As 7 occurs in the long run not less frequently than any other of these outside values, its occurrence on this occasion would not commonly be regarded as very surprising.

x	f
6	0·02
7	0·08
8	0·25
9	0·22
10	0·18
11	0·10
12	0·08
13	0·05
14	0·02
Total	1·00

If the experiment leads to the value 12, no more and no less doubt is engendered than by the occurrence of 7. Either value may be said to lie at the " 0·25 significance level ".

But, using one end of the distribution, it is often said that as values as high as or higher than 12 have the frequency 0·15, therefore 12 is at the " 0·15 significance level ". The implication is that the frequency 0·15 supports the hypothesis while the remaining 0·85 is against it. The fallacy lies in thus setting 7 against 12 whereas these two values have equal frequencies, in setting 6 against 12 whereas 6 has the lower frequency, and so on. Likewise it is argued that as values as small as or smaller than 7 occur with a cumulative frequency of 0·10, so 7 is at the " 0·1 significance level ". Both statements are false, the correct statement being that either 7 or 12 is just outside the 0·75 confidence range, or that either lies at the " 0·25 significance level ".

In the case of a continuous J-shaped distribution such as that of χ_1^2 or of χ_2^2, in which the frequency density is greatest at the value zero of the variate and continually diminishes as the value of the variate increases, the range from 0 to any value of the variate is obviously a confidence range, and the total frequency of values exceeding that value may validly be referred to as the " significance level " corresponding to that value. But this is not valid for a continuous distribution which fades at both ends. For example, in a standard normal distribution, values exceeding +1·96 have the frequency 0·025 ; values from −1·96 to +1·96 form a confidence range with total frequency 0·95 ; values outside this range have the frequency 0·05 ; and either ±1·96 is correctly said to lie at the 0·05, but not the 0·025, " significance level ".

In a symmetrical distribution the limiting values of any confidence range are equal and opposite ; but in a skew distribution, when one limit is given its companion is not found so readily. The frequency density at the value u of the Gamma variate $\frac{1}{2}\chi_{10}^2 \equiv c(5)$ is $\frac{1}{4!}e^{-u}u^4$.[13] If 14 is an observed value of χ_{10}^2 and so 7 is the corresponding observed value of $c(5)$, it can be found (conveniently with a slide rule having a log-log scale) that the f.d. at 2 is about the same as at 7 and thus that 4 to 14 is a rough confidence range for χ_{10}^2. The frequency of values of $\chi_{10}^2 < 4$ is about 0·05, and of values > 14 about 0·17. Hence either 4 or 14 is at the 0·22 significance level.

For sums of squares of larger numbers of statistically independent s.n.v. such as χ_{30}^2, the error in estimating " significance " from one end of the " probability integral " continues to be important—if importance is to be

[13] E.P., p. 217.

measured by the current demand for great accuracy in these matters. For example, the values 18·5 and 40 of χ_{30}^2 have about the same f.d. and form a confidence range. On reference to a table of χ_{30}^2 it is sometimes said that 40 is at the 0·10 significance level nearly, and that 18·5 is at the 0·05 level nearly, whereas either is at the 0·15 significance level, and this gives a quite different basis for either confidence or doubt.

In the same way it follows that the widely used tables of the Variance Ratio (Fisher's z and e^{2z} or F tables)[14] in which, for example, the " upper and lower 5 per cent. points " correspond to the two tails of the same Beta distribution,[15] are liable to the same kind of misinterpretation. For example, when the arguments of these tables, n_1 and n_2, have equal values, then instead of " 5 per cent." we should read " 10 per cent." But when $n_1 \neq n_2$ it will be clear from the preceding paragraphs that we shall often need to use a multiplier larger than 2 to convert to a true significance level the apparent level derivable from these tables.

We may now test the efficacy of the device of using opposite cell numbers in producing confidence ranges by applying the analysis of χ^2 in §II to a simple binomial frequency distribution. A supposedly random sample of 103 individuals is drawn from a very large population in which the proportions of black and white are said to be 10 per cent. and 90 per cent. The sample is found to contain 15 black and 88 white.

Here there are two cells only and $m_1 = 10 \cdot 3$, $m_2 = 92 \cdot 7$; $1/m_1$ and $1/\sqrt{m_2}$ are $O(0 \cdot 1)$. We (tentatively) neglect this order. By (11) the frequency with which α_1 ranges from 14 to its opposite number 7 (the sum of these being the nearest integer to $2m_1$) is to be found approximately by taking $x_1 = 14 \cdot 5 - 10 \cdot 3$, $x'_1 = 4 \cdot 0$, and therefore $x'_2 = -4 \cdot 0$, whence we have opposite values of the s.n.v. $\dfrac{x'_2}{\sqrt{m_2 q_2}} = \pm \dfrac{4 \cdot 0}{3\sqrt{1 \cdot 03}} = \pm 1 \cdot 314$ to determine a confidence range which will just exclude the observed value 15. From the normal table the frequency of values in this range is 0·811 and of values outside it 0·189.

Examining the frequencies of individual values in the appended table of $(0 \cdot 9 + 0 \cdot 1)^{103}$, we see that 7 to 14 is a true confidence range, and also that values outside this range have the frequency $0 \cdot 101 + 0 \cdot 88 = 0 \cdot 189$.

For another example, suppose a sample of 102 contains 16 black. Here $m_1 = 10 \cdot 2$ and from the opposite numbers 15 and 5 we find $x'_2 = -5 \cdot 5$; the s.n.v. has the range $\pm 1 \cdot 815$, and the frequency of values outside this range is 0·070. Comparing this with the binomial table of $(0 \cdot 9 + 0 \cdot 1)^{102}$ we find that 5 to 15 is a true confidence range and that the frequency of values outside it is $0 \cdot 021 + 0 \cdot 046 = 0 \cdot 067$. (In this case one would be disposed to doubt either the technique of sampling or the reputed proportions.)

In these examples the small cell has a mean number as low as 10 nearly, while the large cell, postulated for the argument of §II, is only *moderately* large, its mean number being about 90. Yet the device of opposite numbers provides results which are approximate enough for practical statistical purposes. Exceptions occasionally occur near the centre of the binomial distribution ; for example, the opposite numbers 9 and 12 in a sample of 103 do not form a true confidence range. This would tend to make the reasoning uncertain in the case of several small cells showing observed numbers very near to the mean numbers.

These binomial examples may, of course, also be solved by forming the value of χ_1^2, which gives a solution equally critical with that already found, for here there is but one s.n.v. to be considered. Thus in the first case, the

[14] Fisher and Yates, " Statistical Tables ", Oliver and Boyd, 1938, pp. 30, 31.

[15] E.P., pp. 236, 237.

frequency with which the number in cell (1) is outside the range from 14 to its opposite number 7 is approximately the frequency with which χ_1^2 exceeds $\frac{(4\cdot0)^2}{10\cdot3}+\frac{(4\cdot0)^2}{92\cdot7}=\frac{(4\cdot0)^2}{10\cdot3\times0\cdot9}=1\cdot726$. This frequency may be found from the χ_1^2 table,[16] or, as it is the f. with which the s.n.v. is outside the range $\pm\frac{4\cdot0}{\sqrt{10\cdot3\times0\cdot9}}$, from the normal table as already computed.

Table of Binomial Distributions.

x	$(0\cdot9+0\cdot1)^{100}$ f	$(0\cdot9+0\cdot1)^{102}$ f	$(0\cdot9+0\cdot1)^{103}$ f	$(0\cdot9+0\cdot1)^{105}$ f
2	2	2	2	1
3	6	5	5	4
4	16	14	13	12
5	34	32	29	26
6	60	54	52	47
7	89	83	80	74
8	115	109	107	102
9	130	127	125	122
10	132	131	131	130
11	120	122	123	125
12	99	103	105	108
13	74	79	82	86
14	51	56	58	63
15	33	37	38	43
16	19	22	23	26
17	11	12	13	15
18	5	6	7	8
19	2	3	4	4
20	1	2	2	2
21	1	1	1	1
22	—	—	—	1
Total ..	1000	1000	1000	1000

[16] Yule and Kendall, Theory of Statistics, 1937, p. 535, Appendix, Table 4B.

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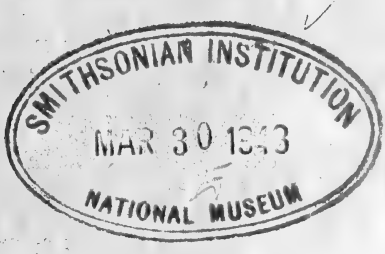

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1942

CONTENTS

VOLUME LXXV

Part III

Page.

ART. IX.—Permian Blastoids from New South Wales. By Ida A. Brown, D.Sc. (Issued October 27, 1941.) 96

ART. X.—Bryozoa from the Silurian and Devonian of New South Wales. By Joan Crockford, B.Sc. (Issued November 27, 1941.) 104

ART. XI.—A Note on Determinations of Physiological Specialisation in Flax Rust. By W. L. Waterhouse, M.C., D.Sc.Agr., D.I.C., and I. A. Watson, B.Sc.Agr., Ph.D. (Issued November 27, 1941.) 115

ART. XII.—The Thiamin (Vitamin B_1) Content of the Urine of *Trichosurus vulpecula*. By A. Bolliger, Ph.D., and C. R. Austin, M.Sc., B.V.Sc. (Issued November 27, 1941.) 118

ART. XIII.—The Chemistry of Bivalent and Trivalent Rhodium. Part I. A Qualitative Study of Trivalent Rhodium Salts; and the Properties of Some Rhodous Salts. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued January 9, 1942.) 122

ART. XIV.—The Chemistry of Bivalent and Trivalent Rhodium. Part II. Hexacovalent Complexes of Rhodous Halides with Diphenylmethylarsine. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued January 9, 1942.) 127

Journal and Proceedings of the Royal Society of New South Wales

VOLUME LXXV

PART III

PERMIAN BLASTOIDS FROM NEW SOUTH WALES.

By Ida A. Brown, D.Sc.,
Department of Geology, The University of Sydney.

(With Plate IV and two text-figures.)

(*Manuscript received, July 23, 1941. Read, August 6, 1941.*)

Abstract.—The paper describes three species of blastoids (two regarded as new) from the Fenestella Beds of the Upper Marine Series (Permian) of the Hunter River District of New South Wales. At least two of these appear to be congeneric with forms from the Basleo Beds of the Permian of Timor, N.E.I.

Introduction.

Examples of recognisable Pelmatozoa are very rare in the Palæozoic rocks of New South Wales. No cystoids are recorded, few blastoids and relatively few crinoids. It is therefore interesting to find specimens of three blastoids, which are possibly congeneric with forms occurring in the Basleo Beds of the Permian of Timor, Netherlands East Indies.

The paper deals with three species belonging to three genera,

Family Codasteridæ Eth. and Carp.

Notoblastus brevispinus gen. et sp. nov.

Family Pentremitidæ d'Orbigny.

Calycoblastus casei sp. nov.

Rhopaloblastus (?) belfordi (Crockford and Brown).

Each species is represented by a single specimen. The first, *Notoblastus brevispinus* gen. et sp. nov., was collected by A. H. Voisey in February, 1941, in a rock specimen exposing only the basal plates, which, on development, yielded a complete specimen.

The second, *Calycoblastus casei* sp. nov., was discovered by E. C. Case of Ann Arbor, in 1923, during a visit to this country, and it was mentioned by T. W. E. David[3] (p. 19), but was subsequently lost. A brief description of it has already been given (Crockford and Brown[2]) based on a plaster cast and photographs of the original specimen. The latter has since been found in the Geological Museum, University of Sydney, and shows certain features not discernible in the cast or photographs, which permit of its more detailed description and its identification with a genus from Timor. An isolated radial plate of the third species was described in the same paper (Crockford and Brown[2]), but its relation to another genus occurring in Timor, *Rhopaloblastus*, is suggested here.

Since no specimens from the Basleo beds of Timor are available to me for examination, comparisons are based entirely on the descriptions and illustrations in papers of J. Wanner.[16, 17, 18] The first species is particularly interesting

MAR - 3 1942

morphologically in showing features that Wanner[16] (p. 185) points out are particularly characteristic of the Permian blastoids of Timor, viz. :

(1) The lengthening of the radials or interradials into arm- or wing-like projections.

(2) The retreat of the ambulacra towards the peripheral parts of the " rays."

(3) The division of the posterior deltoid into a hypo- and epi-deltoid.

Geological Age.

The specimens come from localities twenty miles apart, but all occur in the Fenestella Shales, a bed about 70 to 100 feet in thickness, in the Branxton stage of the Upper Marine Series, which was mapped by L. J. Jones (1932) and found to be consistently 1,500 to 1,600 feet above the Greta Coal Measures.

The Upper Marine Series forms portion of the Permo-Carboniferous or Kamilaroi System (David and Sussmilch,[5] p. 483) of the Hunter River District, New South Wales, which is very fossiliferous on certain horizons. Few, if any, of the species, however, occur outside Eastern Australia, so that correlations are based on general considerations, occurrences of glacial beds, etc., rather than on specific identities in the faunas. The Series occurs between the Lower (or Greta) and the Upper Coal Measures, both of which carry a *Glossopteris* flora.

The Upper Coal Measures have yielded a Labyrinthodont, *Bothriceps major* A. Smith Woodward,[15] regarded as Upper Permian by David ([4] p. 67), and the probable Upper Permian age of the Upper Coal Measures is also indicated by the fairly rich insect fauna described by Tillyard (*in* David,[4] 1932, p. 68).

The age of the *Basleo Beds* of Timor has been discussed by several writers, including J. Wanner,[18] J. Perrin Smith,[14] H. A. Brouwer[1] and De Marez Oyens,[6] and there appears to be consensus of opinion, based chiefly on the occurrence of ammonites, that " the fauna of Basleo agrees fairly well with that of Sosio in Sicily and that of the Word Formation in Texas, in all three regions characterized by the occurrence of *Waagenoceras* " (J. P. Smith[14]).

A. K. Miller[12] has reviewed the stratigraphical significance of all Permian genera of Ammonoids in the Sosio Beds, Sicily, and concludes : " The Permian Sosio beds of Sicily represent a palæontological zone that is slightly but very distinctly younger than the cephalopod-bearing sandstone of the Artinsk group of the Ural Mountains ". He also correlates the Sosio beds with those of Basleo, Timor and the Word Formation of Texas, stating their age to be " almost certainly Middle Permian ".

In a later paper on " Comparison of the Permian Ammonoid Zones of Russia with those of North America ", A. K. Miller[13] places the Word Formation, Texas, with *Waagenoceras*, in the upper part of the Middle Permian. He regards the Artinskian as lower Middle Permian.

In his classic paper " The Type Permian : Its Classification and Correlation ", C. O. Dunbar[7] places the Word Formation, Texas, on the basis of the Fusuline zones, in the upper part of the *Parafusulina* zone, and correlates it with the Kazanian Beds of the Permian of the U.S.S.R.

Unfortunately no fusulinids and only a single specimen of an unidentified ammonoid (Etheridge,[8] p. 36) have been found in the Upper Marine Series in New South Wales.

The occurrence of similar peculiar blastoids in New South Wales and in Timor suggests correlation of the beds in which they occur.

Thus it is suggested that the Fenestella Beds in the Upper Marine Series are approximately equivalent to the Basleo Beds of Timor, and through them are to be correlated with the Sosio Beds of Sicily, the Word Formation of Texas and the Kazanian of the type Permian sequence.

Description of Species.

Phylum ECHINODERMATA.

Class Blastoidea.

Family Codasteridæ Eth. and Carp., 1886.

Genus Notoblastus gen. nov.

Genotype: *Notoblastus brevispinus* gen. et sp. nov. 1½ miles south of Kitchener, near Cessnock, N.S.W.

Diagnosis: Theca discoidal, pentagonal in outline.

Basal cycle, almost flat, pentagonal in outline, consisting of three plates. Radials, five, sharply folded back on themselves at the equator; sinus short, on the upper surface only. Deltoids, five, on the upper surface only. Slightly domed. Posterior deltoid divided into an epi-deltoid and hypo-deltoid, the suture passing across the anal opening. Ambulacra on the upper side of the theca, sub-petaloid, and slightly elevated above the general surface, situated at some distance from the mouth. About 20 side-plates on each side of an ambulacrum. Hydrospire folds cross the radio-deltoid sutures, usually 12 to 14 on each half-suture but apparently none on the radial-hypo-deltoid sutures. Spiracles absent. Mouth central, small, pentagonal. Food grooves radiate to the ambulacra. Anal opening, elliptical and slightly elevated.

Notoblastus brevispinus gen. et sp. nov.

Plate IV, Figures 1-3, Text-figure 1 (*a*, *b*, *c*).

Holotype: Australian Museum, F.39762. Locality: Quarry, 1½ miles south of Kitchener and 4½ miles south of Cessnock, New South Wales. Horizon: Fenestella Shales, Branxton Stage, Upper Marine Series, Permian. Only known specimen is an almost complete theca, collected by A. H. Voisey, 1941.

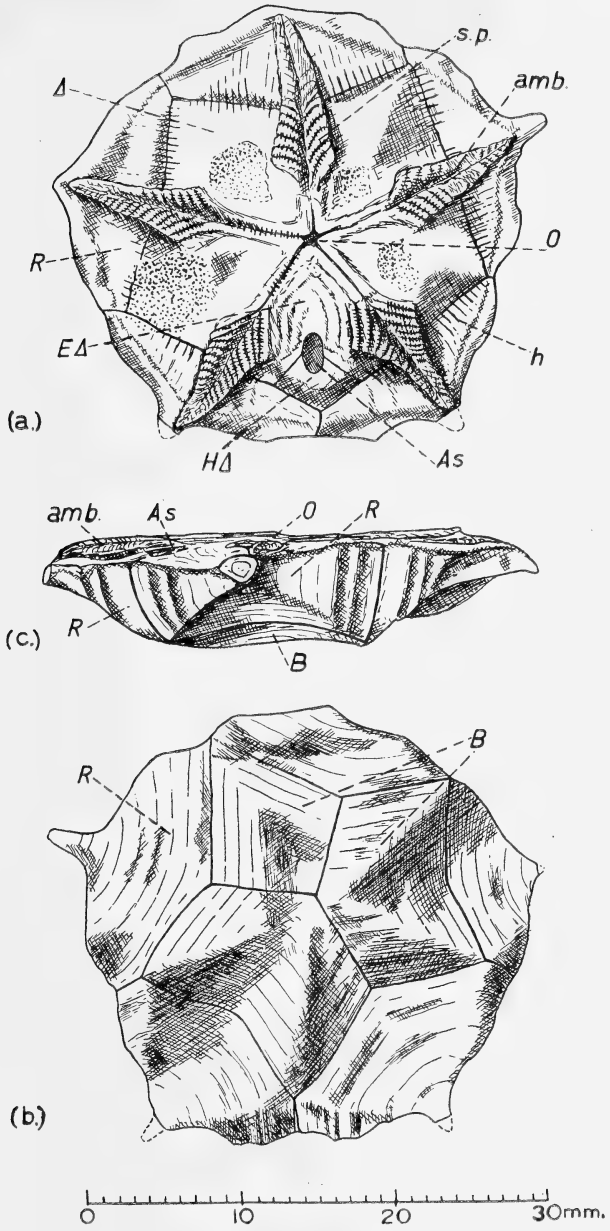
Description. The specimen is a cast in fine sandy shale and has probably been subjected to a certain amount of crushing. Theca very much flattened, pentagonal in outline, the angles being drawn out into short spines. Diameter of theca 30 mm., thickness now from 5 to 7 mm., probably originally more than this.

Basal cycle consists of three plates, one small and two larger plates, pentagonal in outline, a ridge running from the centre to each point of the pentagon. Finely striated parallel to the outer margin. Basal plates 5 to 10 mm. in length. No trace of any stalk.

Radials, five in number, each about 17 mm. in width and 15 mm. in length. The body of each radial is about 10 mm. in length and the limbs 5 mm. The radials are almost doubled back on themselves at the equatorial margin of the theca, and are also drawn out into solid spines up to 3 mm. in length, at the ends of the radial sinuses. Radial sinus short and completely filled with plates of the ambulacra.

Deltoids, five large plates, each quadrilateral and convex upwards. The posterior deltoid divided into an epi-deltoid and a hypo-deltoid by a suture which runs across the anal opening.

Ambulacra, five, petaloid. They commence about one-third of the radial distance from the mouth, equal lengths being situated between the deltoids and in the radial plates. They do not extend on to the spines. Connected to the mouth by a food groove. The ambulacra stand up above the surface of the theca. Lancet plate not visible, completely covered by the side-plates, which are arranged alternately on either side of the central groove. There are about



Text-figure 1.—*Notoblastus brevispinus* g.n. et sp.n. ×2.

Diagrammatic sketch to illustrate structures.

(*a*) Oral view, (*b*) aboral view, (*c*) view of posterior side.

amb., ambulacrum (pseudambulacrum), with food groove ; *s.p.*, side-plates ; *O*, mouth aperture ; △, deltoid ; *E*△, epideltoid ; *H*△, hypodeltoid ; *R*, radial ; *h*, hydrospire-folds ; *B*, basal ; *As*, anal opening.

20 side-plates on each side of each ambulacrum (40 in all). Length of ambulacrum is 10 mm. Length of the side plates : those nearest the mouth about 2·5 mm., those remote from the mouth less than 0·5 mm., inclined to the axis at angles of 50° and 70° respectively. No outer side-plates can be discerned in the specimen.

The anal opening is oval in shape, 1·5 mm. by 3·0 mm., situated two-thirds of the radial distance from the mouth, lying between the epi-deltoid and hypo-deltoid.

Mouth central, small.

Hydrospire folds appear to be represented by a number (14 to 19) of narrow slits which cross the radio-deltoid sutures, and which resemble those in the pectini-rhombs of certain cystoids.

Resemblances. *Notoblastus brevispinus* resembles the *Indoblastus granulatus* Wanner in the general arrangement of the plates, although it differs somewhat in shape, and in the occurrence of short, radial spines. From *Pterotoblastus gracilus* Wanner it differs in general shape, in the position of the ambulacra, the arrangement of the spiracles, and the division of the posterior deltoid into an epi-deltoid and a hypo-deltoid. It differs from *Thaumatoblastus* spp. Wanner in the length of the spines, the situation of the ambulacra, and the number, shape and arrangement of the side-plates. *Thaumatoblastus* is known only by small fragmentary remains and better material may show closer resemblance to the species under consideration.

Family Pentremitidæ d'Orbigny.

Genus **Calycoblastus** Wanner.

Wanner, J., 1924.—Paläontologie von Timor. XIV Lieferung, XXIII Die Permischen Echinodermen von Timor. II Teil, Stuttgart, 1924, pp. 35-40, Taf. CCI, (3), fig. 11-15.

Genotype: *Calycoblastus tricavatus* Wanner. Nordabhang des Somohole bei Soefa, Timor, East Indies.

"Diagnose: Th knospenförmig, am Scheitel zusammengezogen, an der Basis triedrisch, trichterförmig. Querschnitt der Peripherie sub-pentagonal. RR lang und schmal, die Äste viel länger als der Körper. DD klein, aber auf der Aussenseite der Th sichtbar. Ambulakra linear, im Sinus nur schwach eingesenkt. Lanzettstück aussen ganz von den Seitenplättchen, innen von den Hydrospirenplatten bedeckt. Zahl der Seitenplättchen etwa 60. Spirakula 10, von Deltoid- und Seitenplättechen begrenzt; das hintere Paar anscheinend mit der Analöffnung vereinigt. 5 Hydrospirentaschen auf jeder Seite des Ambulakrums."

Calycoblastus casei sp. nov.

Plate IV, Figure 4, Text-figure 2 (*a*, *b*).

Blastoid. T. W. E. David, 1923.—Pan-Pacific Science Congress, Australia, 1923. Guide-Book to the Excursion to the Hunter River District, footnote, p. 19.

Blastoid. J. M. Crockford and I. A. Brown, 1940.—*Proc. Linn. Soc. N. S. Wales*, 1940, 65, p. 168, text-fig. 1, plate IV, figs. 4, 5.

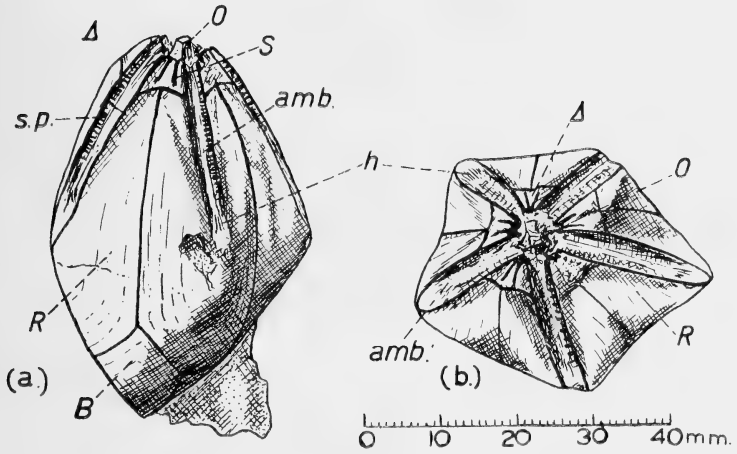
Holotype. Australian Museum, F.39408. Locality: Railway cutting, one mile west of Branxton Railway Station, N. S. Wales. Horizon: Fenestella Shales, Branxton Stage, Upper Marine Series, Permian.

Only specimen known, a cast in fine ferruginous sandstone, collected 1923, by Dr. E. C. Case, in whose honour the species is named.

Description. Theca imperfectly preserved, bud-shaped, about 55 mm. in height; maximum diameter at the base of the radial sinuses, 41 mm. by 26 mm.; equator about half-way between the base and the mouth. Cross-section pentagonal, two straight and three concave sides.

Basal cycle, probably trigonal, the smaller basal (17 mm. long) and portion of one of the larger basals only visible. Funnel-shaped.

Radials, five; each about three-fourths of the height of the theca, convex, 40 mm. in length; ratio of the body to the limbs varies from 20 : 20 to 20 : 25. Interradial sutures straight. Sinus approximately half the length of the plate, with parallel sides, bordered on either side by a narrow triangular bevel, similar to that shown by Wanner for *Calycoblastus tricavatus*. In vertical section the sinus makes an angle of approximately 120° with the body of the radial.



Text-figure 2. *Calycoblastus casei* sp.n.

Diagrammatic sketch to illustrate structures. ×1.

(*a*) Side view, (*b*) oral view.

amb., ambulacrum (pseudambulacrum); *s.p.*, side-plates; *O*, mouth aperture; △, deltoid; *R*, radial; *h*, hydrospire folds; *S*, spiracles; *B*, basal.

Deltoids, five, small, 6 to 7 mm. in length. Radio-deltoid suture convex upwards, so that the shape of the deltoid is a triangle with a concave base. The posterior deltoid, whose position is only partly preserved, probably contained the anus.

Ambulacra, five, from 25 mm. to 30 mm. in length, and of a uniform width of 3 mm. to 4 mm., in grooves 1 mm. to 2 mm. in depth. No side-plates are preserved, but moulds of the side-plates occur at intervals, 20 in a length of 10 mm. on each side of the ambulacrum, indicating in all about 60 on each side of the ambulacrum. Impressions of the underlying lancet plate are exposed in some places, and at the lower ends of two of the ambulacra, impressions of the hydrospire-folds are visible, five on each side of the ambulacrum.

There are indications of 10 spiracles, situated in the inter-ambulacral regions.

Mouth, represented by a protuberance or internal mould, 3 mm. by 2 mm., pentagonal in outline.

Resemblances. The specimen is very close to that of the genotype, *Calycoblastus tricavatus* Wanner, the chief distinction apparently being the ratio of the parts of the radial plates.

From the Carboniferous genus *Tricoelocrinus* Meek and Worthen, 1868, it differs in the shape of the deltoids, the proportions of the radials, the number of the hydrospire folds and the characters of the ambulacra.

Genus Rhopaloblastus Wanner.

Wanner, J., 1924.—Jaarb. Mijnw. Ned.-Oost-Ind. Verh. (1922) 1924, pp. 215-219. Taf. III, fig. 1-5.

Genotype: Rhopaloblastus timoricus Wanner. Basleo, Timor.

" Diagnose : Th keulen- bis birnförmig, an der Basis verlängert, stielförmig, vom Stielansatz bis zu den Radiallippen sich verbreiternd, am Scheitel breit, konvex, im Umriss fünfseitig. Peripherie hoch über dem Aequator, mit den Radiallippen zusammenfallend. Basalkranz hoch, trichterförmig, normal zusammengesetzt. RR gross, kürzer als die BB. Körper der RR mehr als doppelt solang als die Aeste am Radialsinus. DD klein, aber in der seitlichen Ansicht der Th deutlich sichtbar, im Umriss subtrigonal bis rhomboidisch. Ambulakra kurz, lanzettförmig, nur wenig eingesenkt, fast den ganzen Sinus ausfüllend. Lanzettstück von den Seitenplättchen bedeckt. Spirakeln einfach, zuweilen mehr oder weniger vollständig durch ein Medianseptum geteilt, proximal und seitlich von den Seitenplättchen begrenzt ; hintere Spirakeln mit dem Anus zu einer gemeinsamen Oeffnung vereinigt. Hydrospiren auf jeder Seite des Ambulakrums anscheinend drei."

Rhopaloblastus (?) belfordi (Crockford and Brown).

Tricoelocrinus (?) belfordi J. M. Crockford and I. A. Brown, 1940. *Proc. Linn. Soc. N.S.W.*, 1940, 65, pp. 167-170, pl. IV, fig. 1, 2, (?) 3.

Holotype: Australian Museum, F.39158. Locality : 100 yards west of Jump-Up Creek, Portion 14, Parish of Belford, 2½ miles north of Belford Railway Station, New South Wales. Horizon : Fenestella Shales, Branxton Stage, Upper Marine Series, Permian.

Description. There is nothing to add to the description previously given ; the specimen is a single radial plate with portion of the ambulacrum. Other specimens are required to fix its generic affinities with certainty.

Comparison with the described blastoids from the Permian of Timor suggests its relation with *Rhopaloblastus timoricus* Wanner, rather than with the Carboniferous genus *Tricoelocrinus* Meek and Worthen, 1868.

Bibliography.

(1) Brouwer, H. A. : Feestbundel—Dr. K. Martin, 1851-1931. *Leedsche Geol. Mededeelingen*, 1931, Deel V, pp. 558-561.

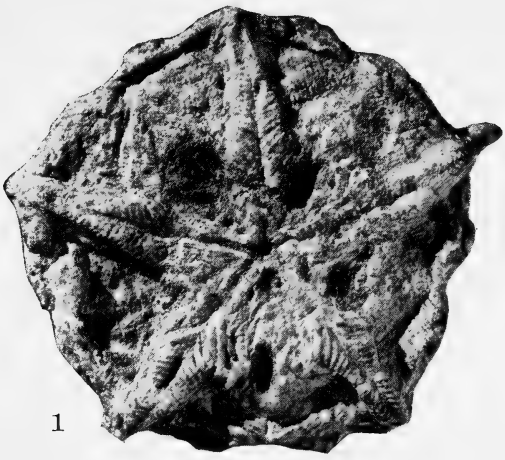
(2) Crockford, J., and Brown, I. A. : A Permian Blastoid from Belford, N.S.W. *Proc. Linn. Soc. N.S.W.*, 1940, *65*, pp. 167-170, pl. iv.

(3) David, T. W. E. : Pan-Pacific Science Congress, Australia, 1923. Guide-book to the Excursion to the Hunter River District, footnote, p. 19.

(4) ———— : Explanatory Notes to Accompany a New Geological Map of the Commonwealth of Australia, p. 67. Aust. Med. Pub. Coy., Sydney. 1932.

(5) David, T. W. E., and Sussmilch, C. A. : Upper Palæozoic Glaciations of Australia. *Bull. Geol. Soc. America*, 1931, *42*, p. 483.

(6) de Marez Oyens, F. A. H. W. : Preliminary Note on the Occurrence of a New Ammonoid Fauna of Permian Age on the Island of Timor. *Koninklijke Nederl. Akad. van Wetens., Proc.*, 1938, *41*, No. 10, 1122.



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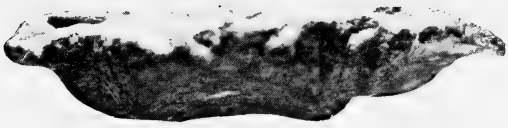

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2

4

[7] Dunbar, C. O.: The Type Permian: Its Classification and Correlation. *Bull. Amer. Assoc. Petroleum Geol.*, 1940, *24*, No. 2, pp. 237-281.

[8] Etheridge, R., Junr.: *Rec. Geol. Surv. N.S.W.*, 1894, *4*, p. 3, pl. VII, figs. 9, 12, 14.

[9] Etheridge, R., Junr., and Carpenter, P. H.: Catalogue of the Blastoidea in the Geological Department of the British Museum (Natural History). 20 plates. London, 1886.

[10] Jones, L. J.: Coal Resources of the Southern Portion of the Maitland-Cessnock-Greta Coal District. *Geol. Surv. N.S.W.*, Min. Res., 1939, No. 37, p. 91.

[11] Meek, F. B., and Worthen, A. H.: *Proc. Acad. Nat. Sci. Philadelphia*, 1868, p. 356.

[12] Miller, A. K.: Age of the Permian Limestones of Sicily. *Amer. Jour. Sci.*, 1933, *26*, pp. 409-427.

[13] Miller, A. K.: Comparison of the Permian Ammonoid Zones of Russia with those of North America. *Bull. Amer. Assoc. Petroleum Geol.*, 1938, *22*, No. 8, p. 1016.

[14] Perrin Smith, J.: Permian Ammonoids of Timor. *Jaarb. Mijn. Ned. Oost-Ind.*, 1926, Verhandelingen, 1-58.

[15] Smith Woodward, A.: On a New Labyrinthodont from Oil Shale at Airly. *Rec. Geol. Surv. N.S.W.*, 1909, *8*, Part 4, pp. 317-319, pl. LI.

[16] Wanner, J.: Die Permischen Blastoiden von Timor. Jaarboek van het Mijnwezen in Nederlandsch Oost-Indië (1922). Verhandelingen, 1924.

[17] ————: Die Permischen Echinodermen von Timor. II Teil. *Paläontologie von Timor*, XIV, Lieferung XXIII. Stuttgart, 1924.

[18] ————: Neue Beiträge der Permischen Echinodermen von Timor. VI. Blastoidea. *Wetensch. Mededeelingen*, No. 16, *Dienst. Mijn. Neder. Indië*, 1931.

Description of Plate IV.

Figures 1-3.—*Notoblastus brevispinus* g.n. et sp.n. ×2. Holotype. Near Kitchener, Cessnock District, N.S.W.

Figure 1.—Theca from the oral side.

Figure 2.—Theca from the aboral side.

Figure 3.—Theca from the side.

Figure 4.—*Calycoblastus casei* sp.n. ×2 approx. Holotype. Near Branxton, N.S.W.

View of portion of theca showing hydrospire folds at lower end of ambulacrum and radio-deltoid suture.

(Photographs by H. G. Gooch.)

BRYOZOA FROM THE SILURIAN AND DEVONIAN OF NEW SOUTH WALES.

By Joan Crockford, B.Sc.

(With Plate V and one text-figure.)

(*Manuscript received, July 2, 1941. Read, August 6, 1941.*)

Contents.

	Page
Summary	104
Introduction	104
Description of Species	105
Acknowledgments	113
Bibliography	113

Summary.

Six new species and one new genus of Bryozoa (Trepostomata and Cryptostomata) are described from the Upper Silurian Hume Series near Yass, and from the Devonian of Taemas (Murrumbidgee River) and Tamworth, New South Wales.

Introduction.

The specimens described were collected from the Upper Silurian near Yass, and from the Devonian near Taemas and Tamworth. The following species of Bryozoa are described:

Order Trepostomata.

Family Heterotrypidæ.

Cyphotrypa (*?*) *shearsbyi* sp. nov. (? Middle Devonian, Taemas) .. p. 105

Order Cryptostomata.

Family Phylloporinidæ.

Pseudohornera (*?*) *retiformis* sp. nov. (Upper Silurian, Yass) .. p. 106

Family Fenestrellinidæ.

Fenestrellina mouara sp. nov. (Middle Devonian, Tamworth) .. p. 108
Semicoscinium vallatum sp. nov. (? Middle Devonian, Taemas) .. p. 109

Family Acanthocladiidæ.

Penniretepora lobata sp. nov. (Upper Silurian, Yass) .. .. p. 110

Family Arthrostylidæ.

Pesnastylus humei gen. et sp. nov. (Upper Silurian, Yass) .. p. 112

Of the genera recorded from the Upper Silurian Hume Series near Yass, *Penniretepora* d'Orbigny has not previously been recorded from below the base of the Devonian; *Pseudohornera* Roemer, to which one species is provisionally referred, ranges from the Upper Ordovician to the Silurian; and species of

Glauconome Goldfuss, to which *Pesnastylus humei* is most closely related, are typically Silurian. *Fenestrellina* d'Orbigny, which is recorded from the Moore Ck. Limestone near Tamworth, ranges from the Early Silurian to the Permian ; the age of the Moore Ck. Limestone (Middle Devonian) has been discussed by Benson.[4] *Semicoscinium* Prout is known elsewhere from the Upper Silurian to the Devonian ; and *Cyphotrypa* Ulrich and Bassler ranges from the Ordovician to the Devonian, but *Cyphotrypa* (*?*) *shearsbyi*, which occurs at Taemas, is most closely related to a Middle Devonian form, *C.* (*?*) *maculosa* Duncan, from the Traverse Group of Michigan. Dr. Hill[9] (p. 249) considers that a Lower Middle Devonian age is indicated by the coral fauna of the limestones at Taemas in which these last two genera occur.

Description of Species.

Phylum BRYOZOA Ehrenberg.

Class Gymnolæmata Allman.

Order Trepostomata Ulrich.

Family Heterotrypidæ Ulrich.

Genus Cyphotrypa Ulrich and Bassler.

Cyphotrypa Ulrich and Bassler, 1904. Smithsonian Miscellaneous Colln., Vol. XLVII, p. 29.

" Massive Heterotrypidæ. Zoœcial walls thin, amalgamated, the central portion light-coloured ; tubes prismatic, with numerous well-developed diaphragms ; mesopores wanting, acanthopores well-developed." (Original definition.)

Genotype : *Leptotrypa acervulosa* Ulrich, 1895, Geol. and N.H. Survey of Minnesota, Vol. III, Pt. 1, p. 318, pl. XXVII, figs. 24, 25.

Cyphotrypa (?) shearsbyi sp. nov.

(Text-figure 1A-B.)

Holotype : 1439, Sydney University Collection.

Horizon and Locality : Basal Limestone Series, (?) Middle Devonian, Por. 229, Par. Waroo, near road about 200 yards north of Taemas Bridge, Murrumbidgee River.

Massive Cyphotrypa (*?*), *with rather thick walls; diaphragms fairly abundant; acanthopores well developed.*

The zoaria are irregular in shape, about 3 cm. in their greatest diameter, and up to 2 cm. in height ; they are composed of more than one layer of tubes, and individual layers may attain a length of over 1 cm. The base of the zoarium is encrusting. The specimens could not be detached from the matrix, and the surface features are therefore not shown ; the presence of monticules is suggested, however, by areas composed of thicker walled tubes ; these areas are up to 3 mm. in diameter, but may be much smaller ; a few irregular, very thin-walled tubes sometimes occur in these monticules, but they have the appearance of abnormal zoœcia rather than of mesopores ; these tubes may have broken down, leaving the centre of the monticule marked by sediment and brown flocculent material. The centres of the monticules are usually at least 4 mm. apart, but as the upper surface of the zoarium was irregular the distance may have been greater at the surface. The zoœcia are sub-angular, usually from 0·2 to 0·3 mm. in diameter, but may be slightly larger at the monticules ; smaller (young) zoœcia are rather infrequently interpolated at the angles of the normal ones. The walls are usually from 0·05 to 0·08 mm. in width, but are slightly thicker

in the monticules, and thinner around the irregular zoœcia. Over a large part of the sections the walls show a fairly broad median light band, bordered by slightly darker material; in some parts, however, the central light band is replaced by very finely granular dark material, or becomes indistinct. The acanthopores, which generally, but not always, occur at the angles of the tubes, are lamellar, and show a fine central lumen; they may slightly indent the tube walls. When the median light band of the walls is replaced by dark granules, these are interrupted by the acanthopores, which are surrounded by a light area. The lamellæ of the acanthopores and walls are best shown in longitudinal sections. The zoœcia over parts of the sections are lined by fine free granules; the infilling of the tubes is usually clear calcite, but may be sediment. The walls are thickened for by far the greater part of their length; for about 0·5 mm. near the base they are, however, thinner, and the tubes may be slightly bent horizontally. Thin, complete, horizontal or oblique diaphragms are developed at irregular intervals in the zoœcia, and from 4 to 12 may occur in 3 mm. There are no cystiphragms. Mesopores are not developed, the occasional smaller tubes shown being young zoœcia.

Remarks: The central light band of the walls resembles that shown in the Heterotrypidæ, but the dark granular band in the centre of the walls over part of the sections is unusual in this family; Cumings and Galloway[5] (p. 359), however, have shown that a median dark band may be developed in the walls of some species of *Heterotrypa*. This species appears to be most closely related to species of *Cyphotrypa* (*?*) such as *C.* (*?*) *maculosa* Duncan, which it resembles in its rather thick walls.

Order Cryptostomata Vine.

Family Phyllodorinidæ Ulrich.

Genus **Pseudohornera** Roemer.

Pseudohornera Roemer, 1876, Leth. Geognostica, 1, Leth. Pal., Vol. I, Atlas, Expl. Pl. XII.

Pseudohornera Roemer, Bassler, 1906, U.S. Geol. Surv., Bull. 292, p. 49.

Pseudohornera Roemer, Bassler, 1911, U.S. Nat. Mus., Bull. 77, p. 172.

Genotype: Retepora diffusa Hall, 1852, Pal. New York, II, p. 160, pl. XL c, Figs. 1*a-f*.

"Zoarium branching dichotomously at frequent intervals, on reverse longitudinally striated; zoœcia in several ranges, tubular, springing from a thin double plate, beneath which a number of vesicles (aborted zoœcia?) are present; vestibules expanding from the orifices to the angular apertures." (Nickles and Bassler, 1900, p. 37, as *Drymotrypa* Ulrich.)

Pseudohornera (?) retiformis sp. nov.

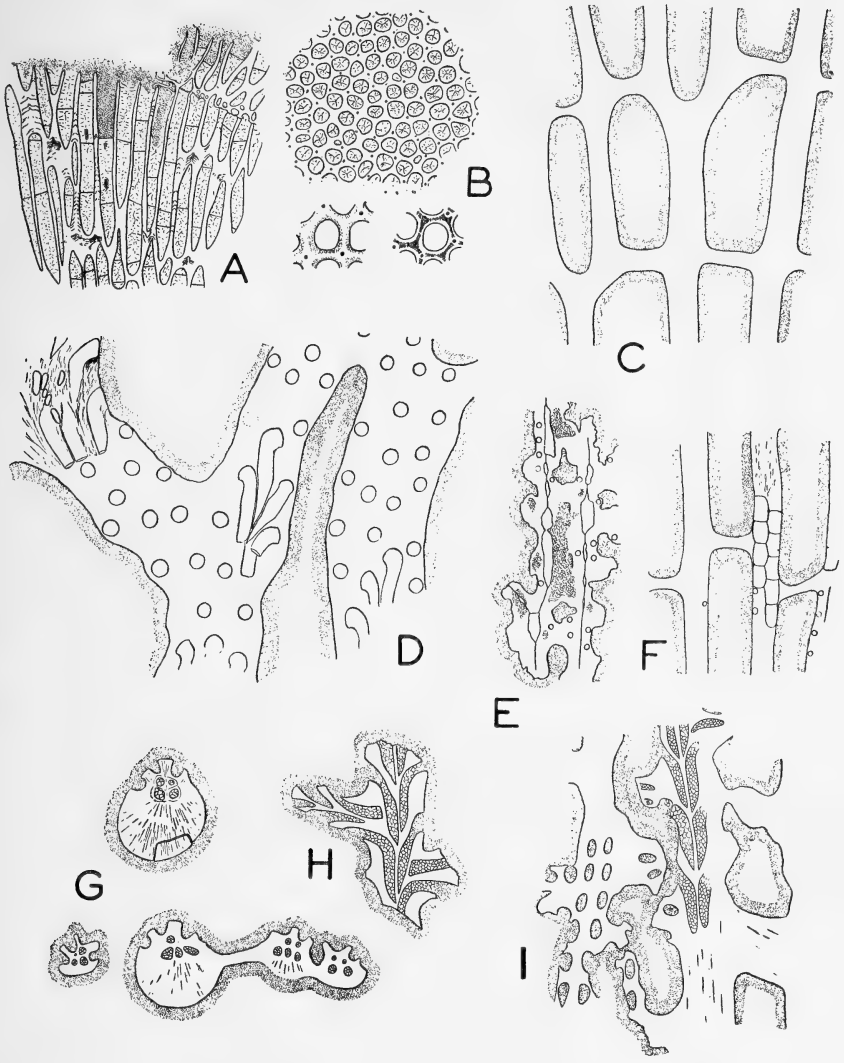
(Plate V, Figs. 4, 5, Text-figure 1d.)

Holotype: F.28532, Australian Museum Collection.

Horizon and Locality: ? Lower Trilobite Horizon, Hume Series, near Bowning.

Reticulate Pseudohornera (?), *with usually three to four rows of zoœcia on each branch; acanthopores and mesopores absent; vesicles developed between the backs of the zoœcia and the reverse surface.*

The holotype is a flat expansion, 3·5 cm. high by 5 cm. wide. The zoarium is reticulate, but there is no indication of the shape of the colony. The specimen is so weathered that no thin sections could be prepared, and the internal structure



Text-figure 1.

A. *Cyphotrypa* (*?*) *shearsbyi* ; vertical section. ×10.

B. *Cyphotrypa* (*?*) *shearsbyi* ; transverse section, ×10 ; and ×20, showing the variation in the structure of the walls of the zoœcia.

C. *Fenestrellina mouara* ; reverse surface of the holotype. ×10.

D. *Pseudohornera* (*?*) *retiformis* ; cast of the celluliferous surface of the holotype, ×10, showing the shape of the zoœcial apertures and of the casts of the zoœcia, and the vesicles developed near the reverse surface.

E. *Semicoscinium vallatum* ; celluliferous surface of a topotype (1441, Sydney University Collection), ×10, showing the expanded carina.

F. *Fenestrellina mouara* ; celluliferous surface of the holotype, ×10.

G. *Pesnastylus humei* ; sections across two midribs, and three lateral branches, ×10.

H, I. *Pesnastylus humei* ; sections parallel to the surface of the branches, showing zoœcia of the lower row on the midrib and lateral branches, and apertures of the upper row, ×10.

is therefore known only from weathered surfaces. The branches are convex on both surfaces, and show usually four, or three, rows of zoœcial apertures; the lateral rows open on the sides of the branches, towards the fenestrules. The branches are from 0·85 to 1·2 mm. in width; the fenestrules, which are very irregularly placed and are irregular in shape, are from 0·5 to almost 3 mm. in width, and from less than 1 mm. to 7 mm.—usually from 3·5 to 6 mm.—in length. The zoœcial apertures are circular, from 0·16 to 0·23 mm. in diameter; no peristomes are shown; the distance between the centres of successive apertures in the same row is from 0·5 to 0·83 mm. The cells are shown as casts, and are elongated and tubular, from about 1·0 to 1·65 mm. in length from their origin to the far side of the aperture; since no sections could be made, the presence or absence of diaphragms could not be determined, but the complete infilling of the zoœcia by sediment suggests that no complete diaphragms were developed. The interspaces between the apertures were thick and are invariably weathered away; no mesopores are shown, though the casts of the zoœcia themselves are well preserved, so that if mesopores did occur it is probable that they were closed at the surface. No acanthopores are developed. The non-celluliferous reverse surface is not well shown; it was not very thick, and seems to have been smooth and evenly rounded. Between the backs of the zoœcia and the reverse surface small vesicles, often elongated, are developed. The basal plate has been weathered away.

Remarks: The presence of vesicles between the backs of the zoœcia and the reverse surface, and also the apparent absence of mesopores, separate this form from species of *Phylloporina* Ulrich, and suggest affinity with *Pseudohornera* Roemer, to which genus it is provisionally referred; the form of the colony, reticulate in this species, instead of dichotomously dividing branches, and the circular apertures—the apertures in *Pseudohornera* are typically angular at the surface, becoming oval within a short distance on account of the thickening of the walls—separate this species, however, from all described species of *Pseudohornera*.

Family Fenestrellinidæ Bassler (Fenestellidæ King).

Genus Fenestrellina* d'Orbigny, 1849.

Homonym: *Fenestella* Lonsdale, 1839, preoccupied for a pelecypod *Fenestella* Bolten, 1798.

Zoarium flabellate or infundibuliform; branches generally straight, sometimes flexuous, connected at regular intervals by dissepiments; apertures in two rows, separated by a plain or tuberculated median keel.

Genotype: *Fenestella crassa* McCoy, 1845, Synopsis of the Carboniferous Limestone Fossils of Ireland, p. 201, pl. 29, fig. 1.

Fenestrellina mouara sp. nov.

(Text-figure 1, c, f.)

Holotype: Specimen 1437, Sydney University Collection.

Horizon and Locality: Middle Devonian (Moore Ck. Limestone), Por. 41, Par. Woolamel, south of Moore (Mouara) Ck., near Tamworth.

Fenestrellina *with from four to twelve—usually about seven—zoœcia to a fenestrule; fenestrules long and rectangular; branches and dissepiments narrow.*

The form of the colony is not shown; the holotype is a fragment about 2 cm. long and 5 cm. wide; there are from rather less than 4, to 5, fenestrules

* An application for suspension of the Rules of Zoological Nomenclature for the generic name *Fenestella* Lonsdale, 1839, has been submitted to the International Commission on Zoological Nomenclature (G. E. Condra and M. K. Elias, Journal of Paleontology, Vol. 15, No. 4 September, 1941), pp. 259-260).

vertically, and from 10 to 11 branches horizontally, in 10 mm. The branches are straight and relatively narrow, from 0·3 to 0·35 mm. in width ; they bifurcate at infrequent intervals and increase to three rows of zoœcia occurs immediately before branching. The celluliferous surface is poorly preserved, but shows a slight median carina ; no nodes could be seen. The apertures are small and circular, about 0·11 mm. in diameter, and are placed on the flattened sides of the branches ; they are separated by almost twice their own diameter, the distance between the centres of successive apertures being about 0·3 mm. ; the number of apertures to a fenestrule varies with the length of the fenestrule, and from four to twelve may occur ; usually there are about seven. The fenestrules are sub-rectangular, from 1·1 to 3·55 mm. (usually about 2 mm.) in length, and from 0·47 to 0·85 mm. in width ; the dissepiments, which expand only slightly at their junction with the branches, are from 0·1 to 0·28 mm. in width. Both branches and dissepiments are evenly rounded on the reverse surface, which seems to have been coarsely granulose ; they are of about the same thickness. The zoœcia are rectangular in outline on the basal plate.

Remarks : From *Fenestrellina propinqua* (de Koninck), a Lower Carboniferous (Burindi) species, this form is distinguished by the more regular shape, and less regular size, of its fenestrules, and by its much broader, thicker branches.

Genus Semicoscinium Prout.

Semicoscinium Prout, 1859, Trans. St. Louis Acad. Sci., Vol. I, p. 443.

" Zoarium funnel-shaped, celluliferous on the outer side ; dissepiments wide, very short, the branches appearing to anastomose on the non-poriferous face, where the fenestrules are sub-rhomboidal or rounded ; apertures in two rows, median keel very high and expanded at the summit." (Nickles and Bassler, 1900, p. 38.)

Genotype : Semicoscinium rhomboideum Prout, 1859, Trans. St. Louis Acad. Sci., Vol. I, No. 3, p. 443, pl. XVII, figs. 1, 1*a-f*.

Semicoscinium vallatum sp. nov.

(Plate V, Fig. 1 ; Text-figure 1E.)

Holotype : 1440, Sydney University Collection.

Horizon and Locality : (?) Middle Devonian (Receptaculites Limestone), Por. 208, Par. Waroo.

Infundibuliform Semicoscinium, *with the celluliferous surface external ; two to three zoœcia to a fenestrule ; carina high, expanded at the summit.*

The zoarium is infundibuliform, with the celluliferous surface external ; expansion of the zoarium commences about 5 mm. above the base of the colony ; near the base the outer surface is covered by a sheath, formed by the coalescence of the summits of the carinæ. There are about 20 branches horizontally, and 14 fenestrules vertically, in 10 mm. The branches, which are from 0·29 to 0·35 mm. in width, show, where they are well preserved, a high median carina, flattened and expanded at the summit, so that the sides of the branches are partly concealed ; over the greater part of the branches, however, the upper part of the carina has been broken away, and it is shown only as a slight ridge along the centre of the branch. No nodes are shown. The zoœcial apertures are placed on the slightly sloping sides of the branches, and are exserted but do not project into the fenestrules ; the apertures are circular, about 0·1 mm. in diameter, and are separated by rather more than their own diameter, the distance between the centres of successive apertures being from 0·23 to 0·29 mm. ; five apertures occur in the length of two fenestrules and two dissepiments, and there are about forty apertures in 10 mm. The fenestrules are oval, from

0·27 to 0·34 mm. in length, and from 0·19 to 0·25 mm. in width; the dissepiments are from 0·29 to 0·4 mm. wide, and the length of one fenestrule and one dissepiment is from 0·62 to 0·72 mm. On the reverse surface both branches and dissepiments are rounded, and they are of about the same thickness. Increase to three rows of apertures occurs immediately before bifurcation.

The zoaria have been replaced by silica, and were etched from limestone; over parts of the surface granular silica has been deposited between the carinæ, but this does not seem to be a replacement of vesicular tissue, such as that developed in the genotype and in *Semicoscinium rhombicum* Ulrich; vesicular tissue does not occur in all species of *Semicoscinium* (Ulrich and Bassler,[24] 1913, p. 285; Prantl,[18] p. 52).

Remarks: This form is distinguished from described species of *Semicoscinium* by its small size.

Family ACANTHOCLADIIDÆ Zittel.

Genus **Penniretepora** d'Orbigny.

Penniretepora d'Orbigny, 1849, Revue et Magasin de Zoologie, 2e Ser., Tome 1, p. 501.

[Non] *Penniretepora* d'Orbigny, 1850, Prodrome de Paléontologie Stratigraphique, Tome 1, p. 45.

Penniretepora d'Orbigny, Bassler, 1934, Fossilium Catalogus, 1, pars 67, Bryozoa, pp. 20, 165.

Homonym: *Acanthopora* Young and Young, 1875 (not d'Orbigny, 1849).

Synonyms: *Glauconome* Auct. (not Goldfuss, 1826). *Pinnatopora* Vine, 1884. *Pinnatopora* Vine and Shrubsole, 1884.

Original Definition: "Deux rangées de cellules d'un seul côté d'un ensemble penniforme, composé d'une tige et de rameaux libres latéraux, non anastimosés."

Genotype: *Retepora pluma* Phillips, 1827, Geol. Yorkshire, pt. 2, p. 199, pl. 1, figs. 13-15.

Penniretepora d'Orbigny, 1849, has priority over *Pinnatopora* Vine and *Pinnatopora* Vine and Shrubsole, 1884. *Penniretepora* d'Orbigny, 1850 (genotype *Glauconome disticha* Goldfuss, Lonsdale) is a synonym of *Glauconome* Goldfuss, 1826, as redefined by Lonsdale in 1839, but many species described as *Glauconome* should be referred to *Penniretepora*.

Penniretepora has not previously been recorded from below the base of the Devonian—d'Orbigny in 1849 gave the range as Silurian to Permian, but was including *Glauconome disticha* in the genus.

Penniretepora lobata sp. nov.

(Plate V, fig. 3.)

[?] "*Pinnatopora*" Shearsby, 1912, Rept. Austr. Assoc. Adv. Sci., Vol. XIII, p. 116.

Holotype: F.30153, Australian Museum Collection.

Horizon and Locality: Barrandella Shales (?), Hume Series, Derrengullen Ck., Por. 10, Par. Yass (holotype); Lower Trilobite Horizon, Hume Series, at the corner of the Bendenine and Boorowa Rds., Por. 12, Par. Derrengullen; Barrandella Shales, Hatton's Corner, Por. 7, Par. Hume.

Penniretepora *with a narrow midrib, from which thin, equidistant branches are given off; zoœcia more closely spaced on the branches than on the midrib.*

The zoarium is pinnate; the midrib is thin, about 0·25 mm. in width, and is straight; lateral branches are given off from both sides of the midrib

at intervals of from 0·85 to 1·0 mm., about 11 branches occurring on each side in 10 mm.; the branches on opposite sides of the midrib are sub-alternating. The branches are straight, and are from 0·19 to 0·25 mm. in width; the longest branch shown reaches a length of 3 mm. and is incomplete. The angle of divergence between the branches and the midrib is about 55° to 60°. Both branches and midrib bear a slight median carina, on which small nodes may be developed; these are not well shown. The apertures are circular, about 0·13 mm. in diameter; they show slight peristomes, and are rather exserted. On the midrib there is one zoœcial aperture at the end of each branch, and one between the branches, the distance between the centres of successive apertures being from 0·43 to 0·51 mm., about twenty-one apertures occurring in 10 mm.; on the lateral branches the distance between the centres of successive apertures is from 0·3 to 0·41 mm., about twenty-seven occurring in 10 mm. On the reverse surface both branches and midrib are rounded, and they show very faint longitudinal striæ; the midrib (which is about 0·25 mm. thick) is much thicker than the branches. Internally the cells are triangular to sub-rhomboidal in outline, and their length equals the distance between their apertures. The inner layer of the reverse surface shows a number of strong longitudinal ridges and grooves.

A specimen of this species from the Lower Trilobite Horizon at the corner of the Bendenine and Boorowa Rds. in Por. 12, Par. Derrengullen (1443, Sydney University Collection), shows a rather more complete zoarium, with a midrib 2 cm. long, and about 0·4 mm. wide near the base and 0·3 mm. wide at the top, from which a number of evenly spaced lateral branches are given off; two of these lateral branches, placed opposite one another, are themselves pinnate, giving off branches up to 2·2 mm. long, and placed the same distance apart as the branches on the midrib; the first of these tertiary branches arises at a distance of from 2·0 to 2·4 mm. from the centre of the midrib. The measurements of this specimen are the same as those of the holotype.

Remarks: From *Pesnastylus humei* sp. nov., this species is distinguished externally by possessing two, instead of four, rows of zoœcia, by its much finer midrib and branches, and there is no anastomosis between the ends of the branches; internally the shape of the zoœcia is very different.

Family Arthrostylidæ Ulrich.

Genus **Pesnastylus** gen. nov.

Zoaria showing no articulation, pinnate, but with the lateral branches from adjacent midribs uniting; new midribs formed by the coalescence of two or more successive branches from adjacent midribs, never by bifurcation of a midrib; stems celluliferous over about one-half of the circumference; zoœcia in four rows, two on each side of a median carina, on both midribs and branches; zoœcia sub-tubular; hemisepta, mesopores, and acanthopores not developed, and diaphragms rarely developed; reverse surface smooth or with faint longitudinal striæ.

Genotype: Pesnastylus humei sp. nov.

No articulation is shown in any of the specimens, and the base of the colony is not shown by any of the zoaria, so that it is possible that either no articulation is developed, as in *Glauconome* Goldfuss, or that articulation is restricted to the base of the colony, as in *Nematopora* Ulrich; other genera of the Arthrostylidæ show very much greater articulation, but very similar zoœcial characters. From *Glauconome* Goldfuss, as redefined by Lonsdale (non *Glauconome* Auct.), this genus is distinguished by the coalescence of the ends of the lateral branches from adjacent midribs, and by the mode of formation of new midribs.

Pesnastylus humei sp. nov.

(Plate V, Figs. 2, 6 ; Text-figure 1, G-I.)

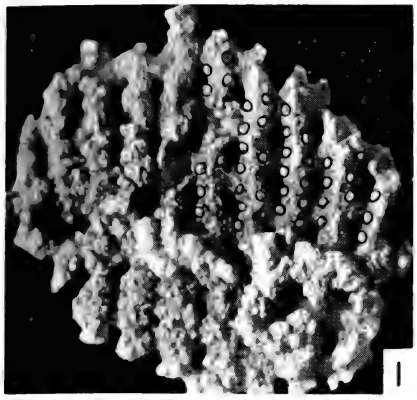
Cotypes: 1445, 1446, Sydney University Collection.

Horizon and Locality: Barrandella Shales, outcrop in small creek west of Taemas Rd., Por. 16, Par. Boambolo (cotypes) ; and Lower Trilobite Horizon, anticline on Boorowa Rd., Por. 12, Par. Derrengullen, and at the corner of the Bendenine and Boorowa Rds., Por. 24, Par. Derrengullen.

Zoarium pinnate, with the ends of the lateral branches from adjacent stems coalescing ; four rows of cells separated by a median carina on both branches and midribs ; reverse surface of midrib very thick, thinner on branches, smooth or with faint longitudinal striæ.

The base of the colony is not shown ; incomplete specimens measure up to 4×7 cm. The zoarium is pinnate, with the ends of the lateral branches from adjacent stems coalescing, and consists of midribs from 0·7 to 1·3 mm. in width, and lateral branches from 0·4 to 0·65 mm. in width ; the lateral branches are given off from the midribs at very variable angles, and may pass straight from one midrib to another, or may point upwards and join to form a new midrib. The distance between adjacent midribs is from 1·5 to 7 mm. The number of branches originating in 10 mm. on each side of a midrib is from 7 to 9 ; the branches on opposite sides of the midrib may be approximately level or may alternate. Both branches and midribs bear a strong, broad, flat-topped median carina, on either side of which are placed two rows of elliptical zoœcial apertures ; on the midrib the apertures of adjacent rows may be placed level or may alternate, and on the branches they are usually alternating. On the midrib three to four apertures of the higher row (next to the carina) and usually one of the lower row occur between the origin of successive branches. The lateral rows of apertures on the branches are placed well down on the sides towards the reverse surface, and are shown only when more than half of the circumference is exposed ; on the midribs the apertures are restricted to the upper half, and the reverse surface is proportionately much thicker ; near the base of the colony extra deposits of calcium carbonate are extensively developed on both surfaces, and may obscure the apertures. The zoœcial apertures are about the same size on both branches and midribs ; they are from 0·24 to 0·3 mm. in length, and about 0·15 mm. in width, and the distance between the centres of successive apertures is from 0·36 to 0·43 mm. in the upper row of the midrib, and from 0·3 to 0·43 mm. on the branches ; the apertures are on the whole rather more closely spaced on the branches ; the spacing of the apertures of the lower row on the midrib depends on the development of the lateral branches. The cell mouths have been filled with sediment, but the greater part of the cells is filled with granular calcite, so that in weathered specimens the casts of the cell mouths are very prominent. The thickness of the midrib is usually between 0·8 and 1·35 mm., and the thickness of the lateral branches about 0·7 mm. The reverse surface is evenly rounded, and may either be smooth or show faint longitudinal striæ.

Internally the four rows of zoœcia are arranged in two vertical series ; the cells gradually move outwards from the centre as they approach their apertures, and are replaced near the centre by new zoœcia. There is no sign of any mesial plate. The zoœcia are elongate and tubular, with rather pointed extremities. Hemisepta are not developed, and diaphragms occur extremely rarely, but may be developed in any part of the zoœcia. The length of a single zoœcium from the tip to the far side of the aperture is from 0·85 to 1·0 mm. on the midrib, and very slightly less on the branches. The apertures are elliptical, but may appear circular where they are cut at a deeper level. The zoœcial walls are unusually thick—about 0·02 mm. Neither mesopores, acanthopores, nor vesicular tissue are developed. The reverse surface shows internally a number of poorly



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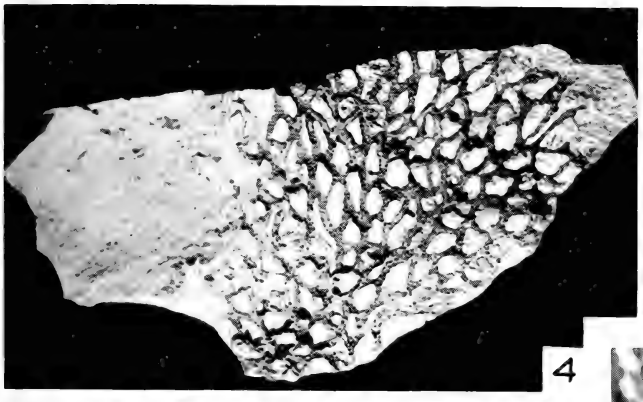

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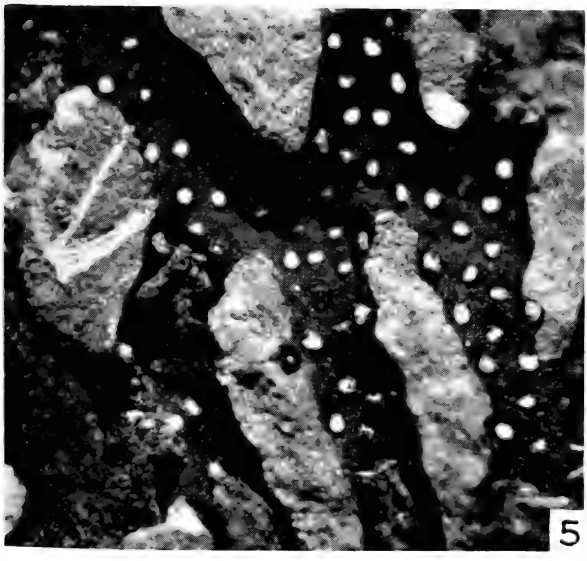

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6

defined longitudinal striæ. The zoœcia shown in Text-figure 1*h* and *i* are those of the lower row on the midrib, which are more widely spaced than usual.

Remarks : This species resembles *Glauconome disticha* Goldfuss in its pinnate form, and in having the zoœcia arranged in four rows, two on each side of a median carina, but differs in size, in its more regular branching, and in the coalescence of the ends of the lateral branches ; internally *Glauconome disticha* shows more numerous diaphragms.

Acknowledgments.

I wish to thank Dr. I. A. Brown for her help in the preparation of this paper, and the Australian Museum for the loan of some of the specimens used in the descriptions. The photographs were taken by Mr. H. G. Gooch. This work has been carried out during the tenure of a Science Research Scholarship at the University of Sydney.

Bibliography.

(1) Bassler, R. S. : The Bryozoan Fauna of the Rochester Shale. *U.S. Geol. Surv. Bull*, 292, 1906.

(2) ———— : The Early Palæozoic Bryozoa of the Baltic Provinces. *U.S. Nat. Mus., Bull.* 77, 1911.

(3) ———— : Fossilium Catalogus, 1, Animalia ; Pars. 67, 1934. Bryozoa.

(4) Benson, W. N. : The Geology and Petrology of the Great Serpentine Belt of N.S.W., Pt. V, The Geology of the Tamworth District. *Proc. Linn. Soc. N.S.W.*, 1915, *40*, Pt. 3.

(5) Cumings, E. R., and Galloway, J. J. : Studies of the Morphology and Histology of the Monticuloporids or Trepostomata. *Bull. Geol. Soc. America*, 1915, *26*, pp. 158, 349-374.

(6) Duncan, Helen : Trepostomatous Bryozoa from the Middle Devonian Traverse Group of Michigan. *Mich. Univ. Mus. Pal. Contr.*, 1939, *5*, No. 10, p. 171.

(7) Goldfuss, A. : Petrefacta Germaniæ, Vol. 1. Düsseldorf, 1827.

(8) Hall, J. : Palæontology of New York, 1852, Vol. II, containing descriptions of the Organic Remains of the lower Middle Division of the New York System. Van Benthuysen, Albany, 1852.

(9) Hill, Dorothy : The Lower Middle Devonian Rugose Corals of the Murrumbidgee and Goodradigbee Rivers, N.S.W. *Jour. Roy. Soc. N.S.W.*, 1941, *74*, p. 247.

(10) Koninck, L. G. de : Recherches sur les fossiles paléozoiques de la Nouvelle Galle de Sud. Mem. Soc. Roy. de Sciences de Liége, 2e Ser., 1877, 8.

(11) ———— : Descriptions of the Palæozoic Fossils of New South Wales. N.S.W. Geol. Surv., Mem. Pal. No. 6, 1898.

(12) Lonsdale, W. : *In* Murchison, Silurian System. London, 1839.

(13) McCoy, F. : Synopsis of the Carboniferous Limestone Fossils of Ireland, 1845.

(14) Nickles, J. M., and Bassler, R. S. : A Synopsis of American Fossil Bryozoa. *U.S. Geol. Surv., Bull.* 173, 1900.

(15) d'Orbigny, A. : Descriptions de Quelques Genres Nouveaux de Mollusques Bryozoaires. Revue et Magasin de Zoologie, 1849, 2e Ser., Tome 1, p. 499.

(16) ———— : Prodrome de Paléontologie Stratigraphique, Tome 1. Paris, 1850.

(17) Phillips, J. : The Geology of Yorkshire, 1827, Vol. 2.

(18) Prantl, F. : Revise Českých Devonskych Fenestellid. *Palœontographica Bohemiæ*, 1932, *15*.

(19) Prout, H. : Fourth Series of Descriptions of Bryozoa from the Palæozoic Rocks of the Western States and Territories. *Trans. St. Louis Acad. Sci.*, 1860, *1*, p. 443.

(19a) Shearsby, A. J. : The Geology of the Yass District. Rept. Aust. Ass. Adv. Sci., Vol. XIII, 1912, p. 106.

(20) Roemer, F. A. : Lethæa Geonostica. I. Lethæa Palæozoica. Atlas, 1876.

(21) Ulrich, E. O. : Palæozoic Bryozoa. *Geol. Surv. Illinois*, 1890, *8*, Pt. 2, Sect. IV.

(22) ———— : On Lower Silurian Bryozoa of Minnesota. *Geol. and N.H. Surv. of Minnesota*, 1895, *3*, Pt. 1.

(23) ————, and Bassler, R. S. : A Revision of the Paleozoic Bryozoa. Pt. II. On Genera and Species of Trepostomata. *Smithsonian Miscellaneous Collections*, 1904, *47*, p. 15.

(24) ———— : Systematic Paleontology of the Lower Devonian Deposits of Maryland, Bryozoa. *Maryland Geological Survey* Lower Devonian, 1913, and Devonian, Plates.

J—August 6, 1941.

Description of Plate V.

Figure 1.—*Semicoscinium vallatum* sp. nov. Celluliferous surface of the holotype. ×10.

Figure 2.—*Pesnastylus humei* sp. nov. Celluliferous surface of a cotype (1445, Sydney University Collection). Natural size.

Figure 3.—*Penniretepora lobata* sp. nov. Cast of the celluliferous surface of the holotype. ×10.

Figure 4.—*Pseudohornera retiformis* sp. nov. Holotype. Natural size.

Figure 5.—*Pseudohornera* (*?*) *retiformis* sp. nov. Cast of the celluliferous surface of the holotype. ×10.

Figure 6.—*Pesnastylus humei* sp. nov. Cast of the celluliferous surface of a topotype (1447, Sydney University Collection), showing the infilling of the mouths of the zoœcia. ×10.

A NOTE ON DETERMINATIONS OF PHYSIOLOGICAL SPECIALISATION IN FLAX RUST.

By W. L. Waterhouse, M.C., D.Sc.Agr., D.I.C.,
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The University of Sydney.

(With Plate VI.)

(*Manuscript received, August 13, 1941. Read, September 3, 1941.*)

Flax rust, caused by *Melampsora lini* (Pers.) Lév., has long been known in Australia as a parasite attacking cultivated flax, *Linum usitatissimum* L. and *L. marginale* Cunn., an indigenous " wild flax ". McAlpine[1] records its occurrence as early as 1885, and states that it is present wherever flax is cultivated.

The rust does considerable damage to seed production under epidemic conditions, but much lighter infections cause serious injury when the crop is grown for fibre. It is for the latter purpose that the present extension of the crop is taking place. Numerous reports of rust damage in varieties which are otherwise suitable for fibre production indicate that a programme for breeding for rust resistance will have to be carried out. For this to be successful a knowledge of the physiological specialisation shown by the pathogen is essential.

Rust fungi frequently show extreme specialisation. Thus in the wheat stem-rust fungus more than 200 physiological races have been determined. Studies of the flax rust have been made extensively in U.S.A. by Dr. H. H. Flor of North Dakota, who has recorded 24 races of the fungus. He has developed a series of differential hosts to sort out physiological races, and kindly made seed available for use in these studies. During the past year Mr. W. W. Poggendorff and other officers of the N. S. Wales Department of Agriculture, together with other workers, have forwarded samples of rusted flax which have been used in the determinations. Our thanks are tendered to them. The technique adopted by Flor[2] has been followed, excepting that no provision was made for a constant light day of 16 hours. Normal hours of daylight have been used.

One of the rusted samples included in the tests was obtained by Dr. E. T. Edwards on *L. marginale* growing near Bourke. The others all came from cultivated varieties of flax growing in the following localities :

N. S. Wales: Leeton (4 collections), Bourke and Macksville.
Victoria: Jindwick.
S. Australia: Mount Gambier (2 collections).
Tasmania: Chudleigh.

In addition to seed of the rust differentials Dr. Flor sent seed of " Bison ", a variety he has found to be susceptible to all the races known to him. At the outset of our work, an attempt was made to use it for the purpose of multiplying the inoculum that was present on the specimens submitted. In no case was any infection obtained. Actually several early collections that were sent in were lost through this failure. As a result the variety " Punjab " is being used in

[1] McAlpine, D. : The Rusts of Australia, 1906, 344 pp., 55 plates. Govt. Printer, Melbourne.

[2] Flor, H. H. : Physiologic Specialization of *Melampsora lini* on *Linum usitatissimum*. *Jour. Agr. Research*, 1935, *51*, 819-839, pl. 1.

place of " Bison " to supply the mother culture from which the differential varieties are inoculated.

It is well known that environmental conditions—and particularly variations in temperature—cause changes in the rust reactions exhibited by particular differential hosts. This becomes a very important consideration in the determination of physiological races. Flor reports that certain of his differential varieties were very sensitive to such changes; one of them was " Williston Brown ". The variety " Akmolinsk " has shown a wide range of variation in our work; the reactions have varied between type " 1 " and type " 3 with chlorosis ". In wheat stem-rust determinations this type of reaction would be styled " 3^{cn} ", and would be indicative of host resistance. Flor[3] states that " attempts to differentiate too finely between degrees of resistance and susceptibility may lead to confusion and to a misunderstanding of results obtained at different localities or under variable conditions ". Keeping this in mind we eliminate minor differences shown in our determinations, and consider that all the collections studied may be regarded as falling within the one physiological race. The typical reactions are as follows:

Differential Variety.	*C.I. Number.*	*Reaction.*
Buda	270–1	R
Williston Golden	25–1	R
Akmolinsk	515–1	SR
J.W.S.	708–1	I
Abyssinian	701	I
Kenya	709–1	I
Williston Brown	803–1	R
" Very pale blue crimped "	647–1	I
Ottawa 770 B	355	I
Argentine	462	I
Bombay	42	S

The letters signify the following reactions: I, immune; R, resistant; SR, semi-resistant; and S, susceptible.

A comparison of these results with those recorded by Flor shows that this race is different from any listed by him. He corroborates this in personal correspondence about the results. Confirmatory evidence is available from two other sources. In the first place the variety " Bison C.I. No. 389 " has been immune in all our tests, although susceptible throughout the U.S.A. investigations. Again, the variety " Argentine C.I. No. 705-1 " which was used in Flor's earlier race determinations (*loc. cit.*) was supplied by him. In our tests it has been immune. He records reactions of 14 races on it. To only one, viz. race 10, was this variety immune. But the reactions of this race on other differentials of the group are quite different from those shown by our rust.

Further work is in progress in which many other varieties of flax are being used. Endeavours are also being made to see whether any race separations can be made from such varied reactions as those shown on " Akmolinsk ". As further collections become available they also will be studied for specialisation.

Conclusion.

Determinations of 10 collections of rust from widely separated areas in Australia have shown that one physiological race is present. This is different from any of the races recorded to date.

Acknowledgment.

Grateful acknowledgment is made of financial assistance from the Commonwealth Research Grant.

[3] Flor, H. H.: New Physiologic Races of Flax Rust, *Jour. Agr. Research, 60*, 575-591.

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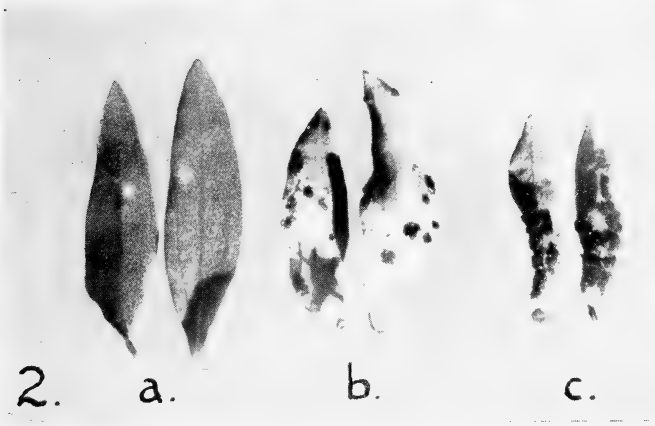

2. a. b. c.

Description of Plate VI.

Fig. 1.—Typical pot of flax seedlings at stage when infection notes are taken. Heavy attack of rust on leaf and stem is present. Five-eighths natural size.

Fig. 2.—Typical rust reactions on pairs of leaves showing:

(*a*) Strong resistance of "Buda" indicated by hypersensitive flecks.

(*b*) Semi-resistance of "Akmolinsk" in which scattered pustules occur in chlorotic and necrotic areas.

(*c*) Susceptibility in "Bombay", showing large confluent pustules and no chlorosis. Magnified 3 times.

THE THIAMIN (VITAMIN B_1) CONTENT OF THE URINE OF *TRICHOSURUS VULPECULA*.

By A. Bolliger, Ph.D.,
and C. R. Austin, M.Sc., B.V.Sc.

(*Manuscript received, August 19, 1941. Read, September 3, 1941.*)

In connection with physiological studies on *Trichosurus vulpecula* (Australian phalanger or possum) some evidence was forthcoming that the urine of this species contained comparatively large amounts of thiamin.[1] This apparent but not fully substantiated " thiaminuria " immediately gave rise to a number of questions, such as the source of the vitamin B_1 and whether or not it was manufactured in this animal's body. Therefore an investigation was undertaken to establish the amount of thiamin excreted in the urine of *Trichosurus vulpecula*.

Experimental.

A. The Collection of Urine.

The animals were placed in metabolism cages and twenty-four hour specimens of urine were collected in the usual manner in bottles containing acid (1 c.c. 20% H_2SO_4). As previously reported,[2] freshly voided specimens from these animals may readily be obtained at almost any time. They could be made to urinate by pressure on the bladder region, and in some cases they were found to micturate spontaneously on being picked up. However, no difference could be observed between the thiamin content of freshly voided specimens and of specimens collected in the metabolism cage. The animals kept in metabolism cages were given prepared diets consisting of lucerne, leaves from certain trees or other food materials.

B. Analytical Methods.

(*a*) *Thiochrome Method.* The principle of this method, originally described by Jansen,[3] lies in the transformation of vitamin B_1 into its fluorescent derivative thiochrome by means of oxidation with alkaline ferricyanide. The fluorescent material is then extracted with butyl alcohol and the resulting solution compared with a similarly treated thiamin standard.

Using the technique described by Wang and Harris,[4] it was soon observed that the thiochrome method was not entirely satisfactory when applied to the analysis of the urine of the phalanger. For example, in spite of the fact that these urines required at least ten-fold dilution prior to assay on account of their high concentration of thiamin, interfering coloured and fluorescent substances often made comparison with the standard difficult. These substances frequently imparted to the butyl alcohol extract a greenish fluorescence in contrast to the blue fluorescence of the standard. For this reason the results could be expressed in increments of not less than 50 micrograms per 100 ml.

Furthermore, it was found that certain substances with a blue fluorescence very similar to that of thiochrome were not extracted by butyl alcohol. The amount of unextracted blue fluorescence was frequently several times larger than that extracted by butyl alcohol (see Table I) and the question arose as to whether all of the thiochrome had been extracted or whether a considerable

part of it was unextractable from this specific medium. Finally, the Moreton Bay Fig leaves eaten by our phalangers produced a blue urinary fluorescence, which was as much as a thousand times stronger than that obtained by butyl alcohol extraction after oxidation with alkaline ferricyanide. Thus a debatable point arose concerning the extent to which this non-extractable fluorescence influenced the fluorescence due to thiochrome.

A further complication was introduced by the fact that the urine of *Trichosurus vulpecula* seems to possess oxidising properties which could apparently convert any thiamin present into thiochrome on the addition of sufficient alkali alone. Pre-treatment with potassium ferricyanide seemed unnecessary, but it was always added as a routine procedure.

(*b*) *Method of Melnick and Field.* In these circumstances it was desirable to employ in addition to the thiochrome method another analytical procedure for the purpose of measuring the thiamin content of the urine of this marsupial. Accordingly, the highly specific method of Melnick and Field[5, 6] was adopted. The principle of this method consists in the coupling of thiamin with diazotised p-aminoaceto-phenone to give a purple-red compound, which is insoluble in water but soluble in certain organic solvents, such as xylene. The xylene solution is used for colorimetric assay. Prior to this reaction the vitamin is removed from the urine by adsorption on zeolite or by extraction with benzyl alcohol. The method was found to be quite suitable for determinations on the urine of *Trichosurus vulpecula* from which good recoveries of added vitamin could be made.

Findings.

Some 25 urines obtained from four different animals were analysed by the method of Melnick and Field as well as by the thiochrome method. Seventeen of these urines were 24-hour specimens. The results from these analyses are listed in Table I. The former method gave values ranging from 255 to 1,630 micrograms per 100 ml., the average rate of excretion being 726 micrograms per 100 ml. In general the thiochrome method gave slightly lower results (varying from 350 to 1,300 micrograms per 100 ml.), particularly in urines with a high thiamin content. With this method the average excretion was at the rate of 650 micrograms per 100 ml.

The average 24-hour output of thiamin as estimated on 17 urines by the method of Melnick and Field was found to be 515 micrograms (range 371 to 1,392 micrograms). With the thiochrome method the average excretion over 24 hours was 452 micrograms.

As already pointed out, these animals when under investigation were kept on a definite diet, the nature of which is indicated in Table I. The diet consisted of leaves from either the Moreton Bay Fig (*Ficus macrophylla*), the Camphor Laurel (*Cinnamomum camphora*) or the Gum tree (*Eucalyptus globulus*), or of lucerne, or bran and pollard and bread. To our knowledge none of these foods is rich in vitamin B_1, and none produced any definite influence on the excretion rate of thiamin. In every instance the urinary excretion of thiamin was large, whether measured by the coupling or by the thiochrome method. It has thus been shown that a phalanger of about 1 to 2 kg. body weight excretes in 24 hours several times the amount excreted by a fully grown man. (The human excretion is reported by Harris *et al.*[7] to be of the order of 35-105 micrograms daily.)

Besides man the thiamin excretion of the rat and the dog have been studied.[8, 9] In both cases it was only a small fraction of that found in the phalanger.

In considering the source of the excreted thiamin one is compelled to assume its synthesis in the animal body to a considerable extent at least. This

TABLE I.

Animal.	Date.	Diet.	Method: Melnick and Field.		Method: Thiochrome.*	
			Micrograms per 100 ml.	Micrograms per 24 hrs. Excretion.	Butyl alc. Extraction. Micrograms per 100 ml.	Without Extraction. Micrograms per 100 ml.
S57	10/5/41	Moreton Bay Fig.	800			300,000
Q1	23/5/41	,, ,, ,,	1,051			
Pr2	2/6/41	Bran and pollard.	400			
S57	2/6/41	,, ,, ,,	700			
Pr2	4/6/41	Moreton Bay Fig.	860	604	700	500,000
S57	4/6/41	,, ,, ,,	560	371	600	400,000
Pr2	5/6/41	,, ,, ,,	1,500	1,295	1,300	
S57	5/6/41	,, ,, ,,	343	412	400	400,000
S57	6/6/41	,, ,, ,,	1,045	1,392	1,100	
Pr2	7/6/41	,, ,, ,,	439	526	500	
S57	7/6/41	,, ,, ,,	255	375	500	
Q1	19/6/41	Bran and pollard.	1,630			1,900
R1	5/7/41	Lucerne.	1,136	397	900	3,000
Q1	5/7/41	,,	1,164	686	800	4,000
R1	6/7/41	,,	384	424	350	1,550
R1	7/7/41	,,	604	531	400	1,800
Q1	7/7/41	,,	443	753	450	1,800
Q1	8/7/41	,,	732	717	600	2,000
R1	9/7/41	,,	588	588	550	1,550
Q1	9/7/41	,,	764	1,278	600	1,600
R1	10/7/41	Camphor Laurel.	1,528	870	1,100	2,500
Q1	10/7/41	,, ,,	1,238		1,000	
Q1	12/7/41	,, ,,	478		600	
Q1	15/7/41	Eucalyptus.	1,366	546	900	2,500
		Pooled urine, bread, bran and pollard.	350			

* As indicated in the text the thiochrome method was carried out with and without the final butyl alcohol extraction. The last two columns in this table contain the results from these two variations.

is borne out by the following example. Two animals were kept for five days on an average daily intake of 120 gms. of Moreton Bay Fig leaves which according to our analyses contained about 100 micrograms of thiamin per 100 gms. But over this period these animals had an average daily thiamin excretion of 714 micrograms. A similar picture was obtained when the phalangers were kept on other food, and, without going further into this aspect on this occasion, we would like to stress our conclusion that this marsupial must manufacture considerable amounts of thiamin.

A few determinations of the fæcal excretion of thiamin indicated that this is small, as in other mammals, and amounts to only about 10% of that of urine.

SUMMARY.

Urinary excretion of thiamin has been studied with the coupling method of Melnick and Field and the thiochrome method. For this particular case it would seem that the thiochrome method is of doubtful validity in view of the very considerable amount of fluorescence which is present in the urine as voided, or which appears on the addition of alkali. The nature of this fluorescence is as yet unknown, but we believe that it is mainly due to some substance other than thiochrome. With both methods the excretion was found to be large irrespective of the diet eaten by the animal, averaging about 500 micrograms per 24 hours.

The amount of thiamin excreted relative to the amount of thiamin ingested with the food leads to the conclusion that the phalanger manufactures thiamin in its body.

The Gordon Craig Research Laboratory,
Department of Surgery, and the
Department of Veterinary Science,
University of Sydney.

References.

(1) Bolliger, A.: *Austral. Journ. Sc.*, 1941.
(2) Bolliger, A., and Carrodus, A.: *Med. Journ. Austral.*, 1938, 1118.
(3) Jansen, B. C. P.: *Rec. Trav. Chim. Pays-Bas*, 1936, *55*, 1046.
(4) Wang, Y. L., and Harris, L. J.: *Biochem. Journ.*, 1939, *33*, 1356.
(5) Melnick, D., and Field, H.: *Journ. Biol. Chem.*, 1939, *127*, 505, 515, 531.
(6) Melnick, D., and Field, H.: *Journ. Biol. Chem,*. 1939, *130*, 97.
(7) Harris, L. G., Leong, P. C., and Ungley, C. C.: *Chem. Ind.*, 1938, *57*, 85.
(8) Light, R. S., Schultz, A. S., Atkin, L., and Cracas, L. J.: *Journ. Nutr.*, 1938, *16*, 333.
(9) Leong, P. C.: *Biochem. Journ.*, 1937, *31*. 367.

THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

Part I. A Qualitative Study of the Effect of Reducing Agents on Trivalent Rhodium Salts; and the Properties of Some Rhodous Salts.

By F. P. Dwyer, M.Sc.,
and R. S. Nyholm, B.Sc.

(*Manuscript received, August 19, 1941. Read, October 1, 1941.*)

Recently, attention was directed by Morgan and Burstall ("Inorganic Chemistry—A Survey of Modern Developments", London, W. Heffer & Sons, 1936, 230) to the surprisingly scant information available concerning bivalent rhodium compounds, of which six examples have been reported. The identity of three of these is extremely doubtful, and in the case of the latter three the rhodous compound appears to have been badly contaminated with the rhodic compound.

The simple chloride $RhCl_2$ and the oxide RhO have been reported by J. J. Berzelius (*Phil. Mag.*, 1829, (2), *5*, 395 *et al.*) as arising from the action of chlorine on rhodium and the pyrolysis of the sesquioxide, respectively. More recently L. Wohler and W. Muller (*Zeit. anorg. Chem.*, 1925, *149*, 125) reported the preparation of these two compounds admixed with the monovalent compounds RhCl and Rh_2O by the pyrolysis of the corresponding trivalent compounds at 965-970°. The reddish brown $RhCl_2$ was separated from the monovalent compound by levigation with carbon tetrachloride. The chloride or the oxide failed to dissolve in hydrochloric acid or water, and no other compounds could be prepared from either. According to J. J. Berzelius the chloride is greyish red, whilst the experience of the present authors is that it is almost black. Similarly, Berzelius (*ibid.*) reported the preparation of the sulphide as a steel-grey powder by either the pyrolysis of the sesquisulphide or the action of sulphur on rhodium. The compound was insoluble in all acids, whilst the experience of the present authors is that it is black, and soluble to a dark red solution in boiling concentrated hydrochloric acid.

Seubert and Kobbé (*Ber.*, 1890, *23*, 2558) isolated a yellow compound to which the formula $2RhSO_3 . 3Na_2SO_3 . 4\frac{1}{2}H_2O$ was assigned. The existence of this compound as a rhodous salt was criticised by Reihlen and Huhn (*Zeit. anorg. Chem.*, 1933, *214*, 189), who showed that the substance was not oxidised by iodine, and was probably a basic rhodic sulphite associated with 2-4 molecules of sodium sulphite. Using various mixtures of sodium sulphite, sodium bisulphite, sodium sulphate, and bisulphate, these latter authors claimed to have isolated the following three compounds: $Na_4(Rh(SO_3)_2 . SO_4)$; $Na_6(Rh_2(SO_3)_4 . SO_4)$; $Na_2(Rh(SO_3)_2)$. The brownish yellow compounds were assigned the above formulæ by the method of ratios, were insoluble in water and organic solvents, but dissolved in dilute hydrochloric, sulphuric and oxalic acids to golden coloured solutions. At higher concentrations of sulphuric acid they dissolved to a redder colour, evolving sulphur dioxide and forming presumably sodium rhodous sulphate. During this research it was noted that rhodous chloride and sulphate were very dark red, and hence it would appear that Reihlen and Huhn in reality isolated sodium rhodic sulphites possibly containing traces only of the rhodous compounds.

Experimental.

The rhodium trichloride solutions used were prepared by solution of the pure metal in potassium bisulphate, precipitation of the oxide and solution in hydrochloric acid. The solution was 1% concentration reckoned as rhodium metal, and was one normal with respect to hydrochloric acid.

The various reducing agents used were found to fall into the following five classes :

Class (*1*). Those that carry the reduction completely to the metal without any indication of an intermediate rhodous stage, viz. chromous chloride in acid solution, alkaline solutions of formic acid, formaldehyde, hydrazine hydrate, and sodium hypophosphite, the metals copper, lead, antimony, bismuth and tin. At room temperature the metal was deposited slowly in brown colloidal form, but at boiling point as a black pulverulent precipitate. Mercury was without effect, as also was silver in the presence of chloride ion. In the presence of iodide ion at boiling point, silver gave a mixture of black rhodium triiodide and rhodium metal.

Class (*2*). Those which under all conditions yield a mixture of rhodium metal and rhodous compounds, viz. sulphurous acid, formic acid, formaldehyde, and silver foil in the presence of bromide ion. No reaction was apparent at room temperature, but on boiling for some time the solution darkened considerably and simultaneously deposited a fine precipitate of rhodium metal. In weakly acid or neutral solution, under the conditions stated by Reihlen and Huhn, sodium sulphite gave a pale yellow precipitate presumably of basic sodium rhodic sulphite, since it was readily soluble in dilute hydrochloric acid to pale orange yellow solutions.

On boiling for two to three hours the basic sulphite precipitate darkened slightly, and then dissolved in hydrochloric acid to a somewhat reddish solution.

Under the latter conditions it would appear that slight reduction to the rhodous state occurred on the surface of the granules.

Class (*3*). The reducing agents of this group may form some rhodium metal, but chiefly dark intensely red solutions of complex rhodous compounds, viz. hypophosphorous acid, sodium hydrosulphite, and sodium formaldehyde sulphoxylate (" Rongalite ").

The reaction with hypophosphorous acid was autocatalytic. No reaction occurred at room temperature, but at the boiling point of the mixture, the solution commenced to darken after about 30 seconds, and then, almost instantly the solution became very dark red. With an amount of reducing agent corresponding to the theoretical equation

$$H_3PO_2 + 4RhCl_3 + 2H_2O \rightarrow H_3PO_4 + 4RhCl_2 + 4HCl$$

the reduction occupied 7-8 minutes at 102° C., but appreciable amounts of rhodium were deposited as metal. With double this amount of reducing agent the reaction was complete in 2-3 minutes at 100° C. An intensely dark red solution resulted, traces only of metal were deposited, and a gas identified as hydrogen was evolved. With an extremely large excess of reducing agent over the latter conditions, the reaction was complete almost instantly at 100°, large volumes of hydrogen gas were evolved, and the dark red solution deposited no rhodium metal even after 8 minutes at 102° C. Proof of the reduction of rhodium to the bivalent state in the above reactions has been afforded by the isolation of analytically pure specimens of tris-diphenylmethylarsine rhodous halides by treating rhodium trihalides with the arsine, the corresponding halogen acid, and hypophosphorous acid. These compounds will be described in a subsequent communication. Curiously enough, addition of the arsine and a halogen acid to solutions of rhodium trichloride previously reduced with hypophosphorous acid gave only very small amounts of tris-diphenylmethylarsine rhodous halide. This suggested that the rhodium after reduction with hypophosphorous acid was bound in some form of a complex. This view was supported by the failure to prepare derivatives of bivalent rhodium by the addition of 8-hydroxy quinoline or ethylenediamine bis-salicyaldehyde. Similarly, the simple sulphide RhS could not be prepared by passage of hydrogen sulphide except under such conditions of acidity that much rhodous phosphate or phosphite was co-precipitated.

By using alkaline sodium hypophosphite and alkali rhodicyanide, Manchot and Schmid (*Ber.*, 1931, *63*B, 1872) obtained a colourless solution with strong reducing properties, which were attributed to monovalent rhodium present as $Na_2Rh(CN)_3$. It was found that the reaction

could be performed easily, but on acidification a very dark red solution resulted. Since this colour was found to be characteristic of bivalent rhodium compounds, it would appear that the substance prepared by Manchot and Schmid was probably $Na_4Rh(CN)_6$ containing bivalent rhodium and analogous to sodium cobaltocyanide. Some indications of monovalent rhodium were noted in the reductions performed with hypophosphorous acid. With an excess of the reducing agent, and heating to 100° until a violent evolution of hydrogen gas commenced, followed by rapid cooling in ice, a brownish yellow solution resulted which acted as an extremely powerful reducing agent. This solution probably contained monovalent rhodium and the evolution of hydrogen gas is due, it is suggested, to reaction between the mineral acid and the monovalent rhodium salt, which thereby passes to the bivalent state

$$2RhCl + 2HCl \rightarrow 2RhCl_2 + H_2.$$

In hot hydrochloric acid, Asmanow (*Z. anorg. Chem.*, 1927, *160*, 209) has noted that solutions of chromous chloride are oxidised to chromic chloride with the evolution of hydrogen gas.

Finally, it was noted that the reduction with hypophorous acid was catalysed by traces of copper of the order of 1%, but seemed to be inhibited by larger amounts of the order of 5% of the rhodium being used. The reduction was also inhibited by concentrated mineral acids.

In hydrochloric acid solution from 1 N to 5 N rhodium trichloride was reduced instantly at room temperature by sodium hydrosulphite to an intense red colour recalling the colour of concentrated ferric thiocyanate. Instantly at 100° and slowly at room temperature, the reduction proceeded to the metal. The reaction could be performed on sodium rhodite at 80° but the resultant precipitate which was dark brown, was only partly soluble in acid, and was contaminated with rhodium metal. The dark red solution appeared to contain a complex sodium rhodous sulphite, which could be precipitated with alcohol, but no simple derivatives such as the sulphide or the 8-hydroxyquinolate could be prepared from it.

Sodium formaldehyde sulphoxylate even when present in large excess reduced rhodium trichloride at 40° C. to an intense ruby red coloured solution. Addition of alcohol precipitated a dark red powder, which was completely soluble in water, contained sodium, rhodium, formaldehyde and sulphite, and was decomposed by iodine, or hydrogen peroxide. No simple rhodous salts could be prepared from this complex.

Further investigation on the reducing agents in this group is proceeding.

Class (*4*). Those that carry the reduction to the rhodous state only, but owing to the slow rate are impracticable except in inert atmospheres, viz. acid solutions of hydroxylamine chloride or sulphate, and the corresponding hydrazine salts. The reduction was found to occur only at boiling point, and was catalysed by a trace of cupric chloride, which was apparently reduced instantly to the cuprous state and then acted as the reducing agent for the rhodium. Curiously enough hydroxylamine hydrate failed to reduce sodium rhodite at 100°, the resulting yellow precipitate of rhodium sesquioxide containing no trace of either rhodium metal or rhodous oxide.

Solutions of cuprous chloride are well known for the reduction of chloroplatinates to chloroplatinites. With rhodium trichloride the reduction to the rhodous state did not proceed beyond about 20%, and it is suggested that the reaction

$$RhCl_3 + CuCl \rightarrow RhCl_2 + CuCl_2$$

rapidly reaches an equilibrium—i.e. that the oxidation-reduction potential of the reaction $Rh^{3+} + e \rightarrow Rh^{2+}$ is of the same order as that of the reaction $Cu^{2+} + e \rightarrow Cu^{+}$ (0·21 volts). This observation is supported by the fact that solutions of rhodous chloride prepared by another method only partly reduced cupric chloride solution, and by the failure of the arsine stabilised rhodous halides to yield more than a trace of cuprous chloride by reaction with alcoholic cupric chloride solution. The copper salt catalysed reaction with hydroxylamine hydrochloride apparently depended upon the continuous reduction of cupric ions preventing their accumulation in the solution.

Class (*5*). Those that carry the reduction completely to the rhodous state without complex formation or the production of any rhodium metal, viz. stannous chloride and sodium stannite. According to J. J. Berzelius (*loc. cit.*), addition of stannous chloride to rhodium trichloride solution yielded a pale yellow precipitate easily soluble in excess acid to a yellow solution. N. W. Fischer

(*Schweigger's Journ.*, 1889, *53*, 117, 173) claimed that a yellow or brown precipitate or a brown solution resulted depending on the acid concentration. More recently, W. Singleton (*Ind. Chemist*, 1927, *3*, 121) advanced the reaction as a test for rhodium. At boiling point it was claimed that a brown colloidal solution resulted, and ultimately a fine crimson colour recalling Purple of Cassius.

It has now been found that addition of weakly acid stannous chloride to almost neutral rhodium trichloride solution gave a fine yellow precipitate instantly at room temperature. At 100° for a few seconds, the precipitation was complete, and the residual solution was found to be free of rhodium and almost free of tin. The precipitate varied in colour from yellow to orange, and conformed to no fixed composition. The same types of precipitate could be prepared by the addition of stannous hydroxy-chloride to almost neutral rhodium trichloride. The substance was freely soluble in hydrochloric acid to orange yellow solutions, and consisted undoubtedly of mixtures of basic stannous and rhodic chloride. When the mixed basic salts were heated with water at 100° for fifteen minutes, the colour darkened considerably, and the precipitate then dissolved in hydrochloric acid to a dark red solution. Addition of sodium sulphate to this solution at boiling point precipitated some of the tin as stannic oxide, hence it is concluded that the dark precipitate consisted of a mixture of the basic salts of rhodous, rhodic, stannous and stannic chlorides.

In hydrochloric acid solution above a concentration of 2 N mixtures of stannous and rhodic chloride gave no precipitate on boiling, but after a few minutes the colour darkened, changing at the end of four minutes to an intense red. No metal was deposited, and there was no evidence to suggest that any metal was in the colloidal form. By the addition of tertiary arsines to the red solution, it has been possible to prepare pure specimens of the compounds $RhCl_2 . 3AsR_3$, and $RhCl_2 . SnCl_2 . 3AsR_3$, which will be described in a subsequent communication.

At room temperature sodium stannite was without effect on sodium rhodite but at 70-80° the colour changed to dark red and a dark red precipitate of indefinite composition consisting of rhodous hydroxide, stannic hydroxide and sodium stannate was deposited. At boiling point this precipitate changed in colour to almost black, due it is considered to the decomposition of the rhodous hydroxide to the hydrated oxide. Both the dark red and the black precipitate were soluble in hydrochloric acid to dark red solutions.

$$Na_2SnO_2 + 2NaRhO_2 + 3H_2O \rightarrow Na_2SnO_3 + 2NaOH + 2Rh(OH)_2$$
$$Rh(OH)_2 \rightarrow RhO + H_2O$$

All attempts to free the above preparations from tin salts have failed. Tests on samples of rhodous hydroxide and oxide after ten washings with hot caustic soda in an apparatus filled with nitrogen, showed them still to be contaminated with stannic tin. Since stannic sulphide normally does not precipitate in hydrochloric acid solution above 0·5 N, attempts were made to prepare pure rhodous sulphide by passage of hydrogen sulphide through solutions of rhodous hydroxide in 8 N hydrochloric acid. Stannic sulphide, however, was co-precipitated. This behaviour recalls the co-precipitation of cadmium sulphide with mercuric sulphide in strongly acid solution, in which cadmium sulphide alone would fail to precipitate. (Feigl, *Mikrochem.*, 1923, *1*, 4.)

The Properties of Some Rhodous Salts.

Despite the unfortunate contamination with tin, it is considered valuable to indicate some of the properties of a few simple rhodous salts. The salts were prepared from rhodous hydroxide after ten washings with hot normal caustic soda, and contained approximately 10% tin as the stannic salt.

Rhodous chloride was a black hygroscopic solid, and contained water of crystallisation. It was hydrolysed instantly by water, yielding an orange basic salt, but dissolved in hydrochloric acid to a dark red solution, which absorbed oxygen from the air with a progressive decrease in colour. Solutions of mercuric chloride were reduced slowly at room temperature to mercurous chloride, but instantly at boiling point to black mercury. Cupric chloride was only partly reduced at boiling point. Nitric acid oxidised rhodous chloride on warming, but hydrogen peroxide and potassium permanganate instantly at room temperature. On prolonged boiling in an inert atmosphere solutions of rhodous chloride underwent self oxidation and reduction with lightening

of colour and the separation of metallic rhodium. Addition of sodium, potassium, ammonium or rubidium chlorides failed to precipitate a complex chloride.

Rhodous bromide and iodide were soluble salts similar to the chloride although darker in colour. Rhodous iodide was extremely soluble in water to an intense purple solution, which rapidly oxidised in the air with the separation of the black insoluble rhodic iodide. Rhodous oxide and hydroxide were not so sensitive to oxidation as the chloride, but showed no amphoteric properties like the corresponding rhodic compounds.

Rhodous sulphide was precipitated from solutions of the chloride by passage of hydrogen sulphide in acid concentrations up to 8 N. The black flocculent precipitate was dark reddish brown by transmitted light, but settled to a fine black precipitate on heating for a few minutes at 100° C. It was insoluble in ammonium sulphide, but dissolved slowly in boiling concentrated hydrochloric acid to a dark red solution with the evolution of minute bubbles of hydrogen sulphide. The substance was easily soluble in dilute hydrochloric acid in the presence of a minute trace of nitric acid, but with higher concentrations of nitric acid the orange rhodic chloride was formed.

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THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

Part II. Hexacovalent Complexes of Rhodous Halides with Diphenylmethylarsine.

By F. P. Dwyer, M.Sc.,
and R. S. Nyholm, B.Sc.

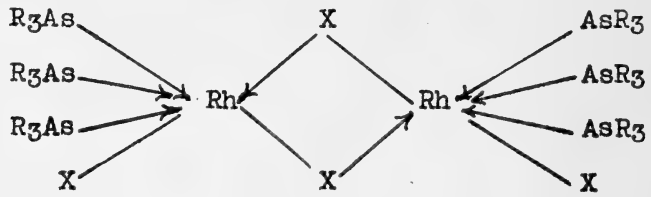
(*Manuscript received, August 19, 1941. Read, September 3, 1941.*)

In the previous paper (This Journal, 1941, 122) evidence was adduced to show that trivalent rhodium salts were capable of reduction to the bivalent rhodous state by a variety of reducing agents, but owing to the difficulty of purification of the reduced products, no analytically pure compounds could be isolated. In accordance with the well accepted principle that unstable valency states might be stabilised by suitable coordinating groups, a great number of substances were tested including 8 hydroxyquinoline, thiourea, ethylenethiourea, thioglycollic acid, dithiooxamide, and a number of tertiary arsines. Although evidence was obtained of complex formation in all cases, the latter series of substances proved the most suitable. These latter compounds have been studied extensively by Burrows and his co-workers (This Journal, 1940, *74*, M 14), have been found to coordinate readily with a great variety of metallic salts, and further possess the excellent property of being mild reducing agents because of the tendency of trivalent arsenic to pass to the tetracovalent state. For instance, cupric chloride is reduced to cuprous chloride, which may be isolated as complex with the excess tertiary arsine (Burrows and Sandford, *ibid.*, 1935, *69*, 182).

When rhodium trichloride is heated with a tertiary arsine in alcoholic solution, the arsine coordinates fairly slowly and soluble rhodic coordinated compounds may be isolated in which the metal exhibits a coordination number of six. Even on continued boiling with alcohol these rhodic compounds, which will be described in detail in a subsequent paper, show no tendency to undergo reduction. However, they may be easily reduced with hypophosphorous acid in strongly acid solution and the insoluble rhodous complexes isolated in crystalline form. Curiously enough, if a rhodic salt such as rhodic chloride is previously reduced with hypophosphorous acid and the arsine then added in the presence of a large excess of concentrated hydrochloric acid, there is no evidence of complex formation and the arsine may be recovered unchanged. This effect is due no doubt to the formation of a stable rhodous hypophosphite complex, which is unaffected by even concentrated hydrochloric acid.

The arsine compounds described in this paper are coloured crystalline solids, with sharp melting points. The colour darkens progressively as the compounds pass from chloride to iodide. They are insoluble in water, and ionising solvents such as alcohol, and yield no precipitate of the silver halide on treatment with silver salts. This latter fact coupled with their relatively low melting points, and ready solubility in organic solvents such as chloroform or benzene, suggest that they are completely covalent. They possess the general formula $Rh \cdot X_2 \cdot 3((C_6H_5)_2Ch_3As)$ and are dimeric in boiling chloroform. In the proposed structure (I) the rhodous metal is given a coordination number of six, and the molecule is bridged by chlorine atoms in the well-known manner of

aluminium chloride, and the compounds of cuprous and cupric chlorides, and palladous chloride with tertiary arsines and phosphines.



Experimental.

Tris-diphenylmethylarsine Rhodous Chloride. Rhodium trichloride 0·13 g. dissolved in water 20 mls., was treated with diphenyl methyl arsine 0·9 g. dissolved in ethyl alcohol 120 mls., and concentrated hydrochloric acid 15 mls., and 30% hypophosphorous acid 1·5 mls. added. The mixture was refluxed until at the end of 40 minutes the bumping due to the precipitation of solid became very violent. After cooling, the brown crystalline precipitate was removed, washed with alcohol and water several times, and dried in the steam oven at 100° C. The compound may be crystallised from hot benzene. It crystallised in leaflets and rhombs, and by reason of the square twinning the crystals belong probably to the rhombic system. On heating the substance melted sharply at 171° to a black liquid which then evolved arsine and left a black or silvery residue of rhodium. The compound was insoluble in water and alcohol, very sparingly soluble in hot acetone, but easily soluble in warm benzene and chloroform to a red solution. In acetone or pyridine, the compound reduced silver nitrate to the metal, almost quantitatively, and mercuric chloride to mercurous chloride. In cold pyridine the reduction of silver nitrate was instantaneous (even in boiling acetone the arsine itself does not reduce silver nitrate).

The compound was stable to boiling concentrated hydrochloric acid, and cold caustic alkali, but the latter reagent at 100° liberated the arsine and left a black tarry residue.

The substance was analysed for rhodium by ignition, slowly at first to remove arsine, then at bright red heat in an oxidising atmosphere, and finally in a reducing atmosphere. This latter condition was easily realised by fitting the crucible with an oversize lid. The residue of metallic rhodium was always a bright silvery colour. The halogen was estimated by distillation of the compound with concentrated sulphuric acid, and absorption of the acid in standard silver nitrate solution. This method, which will be described later in detail, was checked by estimation of the halogen by the method of Burrows and Lench (This Journal, 1936, *70*, 218).

Found: Rh, 11·28%; Cl, 7·68%; mol. wt. (Chloroform, ebullioscopic), 2030, 1597.

Calculated for $[RhCl_2 . 3(C_6H_5)_2 . CH_3 . As)]_2$: Rh, 11·35%; Cl, 7·83; mol. wt., 1812.

(After boiling with chloroform for some time a slight precipitate separated, due no doubt to oxidation. This probably accounts for the lower molecular weight in the second determination.)

Tris-diphenylmethylarsine Rhodous Bromide. A solution of rhodium trichloride containing 0·216 g. of rhodium was treated with excess of sodium carbonate, and boiled for some time to precipitate the hydroxide completely. The yellow precipitate after washing was dissolved in 15 mls. of 10 N hydrobromic acid, and diphenylmethylarsine 1·52 g., alcohol 150 mls. and hypophosphorous acid (30%) 1·5 mls. added. After refluxing as before, the solution darkened at the end of three minutes, and the compound commenced to precipitate. The reaction was complete in sixteen minutes. The reddish brown leaflets melted at 180° C., and were insoluble in alcohol, very sparingly soluble in hot acetone, but easily soluble in hot chloroform to a red solution. As before, silver nitrate solution was reduced to metallic silver.

Found: Rh, 10·27%; Br, 16·03%.

Calculated for $[RhBr_2 . 3(C_6H_5)_2 . CH_3 . As)]_2$: Rh, 10·34%; Br, 16·06%.

Tris-diphenylmethylarsine Rhodous Iodide. Owing to the insolubility of rhodium triiodide in water, the method used for the preparation of the bromide was not available. A solution of rhodium trichloride containing 0·0864 g. of rhodium dissolved in 10 mls. of water was treated with 10 mls. of 64% hydriodic acid, previously just decolorised with hypophosphorous acid, and

immediately with 0·76 g. of diphenylmethyl arsine dissolved in 100 mls. of ethyl alcohol. The resulting dark solution of tris-diphenylmethylarsine rhodic iodide was then reduced by refluxing with 1·5 mls. of 30% hypophosphorous acid. At the end of 30 minutes the dark brownish red precipitate was removed. The substance, like the chloride and the bromide, crystallised in leaflets, m.p. 168° C., and was insoluble in water and alcohol, but dissolved easily in chloroform to a dark red solution. A suspension in hot acetone rapidly reduced silver nitrate to the metal.

Found: Rh, 9·34%.

Calculated for $[RhI_2 . 3(C_6H_5)_2 . CH_3 . As)]_2$: Rh, 9·45%.

Summary.

The preparation of three rhodous halides stabilised with diphenylmethylarsine is described. The compounds are shown to be dimeric and to act as powerful reducing agents.

Acknowledgment.

The authors are indebted to Mr. D. P. Mellor for making available samples of diphenylmethylarsine and other tertiary arsines.

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CONTENTS

VOLUME LXXV

Part IV

ART. XV.—Radial Heat Flow in Circular Cylinders with a General Boundary Condition. II. By J. C. Jaeger, M.A., D.Sc. (Issued April 22, 1942) 130

ART. XVI.—The Chemistry of Bivalent and Trivalent Rhodium. Part III. Compounds of Rhodic Halides with Tertiary Arsines. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued April 21, 1942) 140

ART. XVII.—The Triassic Fishes of New South Wales. By R. T. Wade, M.A., Ph.D. (Issued April 22, 1942) 144

ART. XVIII.—Studies on the Cultivation of the Tung Oil Tree, *Aleurites fordii*. Part II. Study of a Heavy Yield of Fruit Obtained on the North Coast of New South Wales. By A. R. Penfold, F.A.C.I., F.C.S., F. R. Morrison, A.S.T.C., A.A.C.I., and S. Smith-White, B.Sc.Agr. (Issued April 22, 1942) 148

ART. XIX.—The Stereochemistry of Some Metallic Complexes, with Special Reference to their Magnetic Properties and the Cotton Effect. By D. P. Mellor, M.Sc. (Issued April 21, 1942) 157

ART. XX.—On the Frequency of the Primes. By F. A. Behrend. (Issued May 15, 1942) 169

TITLE PAGE, CONTENTS, NOTICES, PUBLICATIONS i

OFFICERS FOR 1941-42 vii

LIST OF MEMBERS, AWARDS OF MEDALS, ETC. ix

ABSTRACT OF PROCEEDINGS xxi

PROCEEDINGS OF THE SECTION OF GEOLOGY xxx

PROCEEDINGS OF THE SECTION OF INDUSTRY xxxi

INDEX TO VOLUME LXXV xxxiii

Journal and Proceedings of the Royal Society of New South Wales

VOLUME LXXV

PART IV

L—October 1, 1941.

RADIAL HEAT FLOW IN CIRCULAR CYLINDERS WITH A GENERAL BOUNDARY CONDITION. II.

By J. C. JAEGER, M.A., D.Sc.

(Communicated by Professor H. S. Carslaw.)

(*Manuscript received, August 1, 1941. Read, October 1, 1941.*)

1. In these Proceedings[1] a number of results were given on conduction of heat in regions bounded internally or externally by circular cylinders with boundary condition

$$k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3 v=k_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

at a surface. The solutions were obtained by a formal method using the Laplace transformation and it was remarked that it could be verified by a procedure previously developed elsewhere[2] that they did in fact satisfy the differential equations and boundary and initial conditions of their problems. The verification procedure described in II is applicable to a wide range of one-variable problems in conduction of heat, and, since only some special problems of those in III were verified, it seems worth while indicating that the complete set of results obtained in I may be verified in this way. These include most of the results of III as special cases.

In §§2, 3, 4 three results on the nature of the roots of certain equations involving Bessel functions, which were stated without proof in I and are of intrinsic interest, will be proved for a set of conditions including those of physical interest in I.

2. *The Roots of the Equation.*[3]

$$(lz^2-m)J_0(z)+nzJ_1(z)=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where l, m, n *are real constants, are all real and simple (except possibly for* z$=0$*) provided*

$$l\geqslant 0,\ m\geqslant 0,\ n>0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

In (2) we may without loss of generality take $l\geqslant 0$ and if $l=0$ we take $m>0$. This convention is implied, here and subsequently, in stating results such as (3), (6) and (8).

If some of l, m, n vanish the equation (2) reduces to a simpler form. If $l=m=0$ the result is well known. If $n=0$ the equation becomes $(lz^2-m)J_0(z)=0$, which if $l>0$, $m>0$, may have double roots at $\pm(m/l)^{\frac{1}{2}}$, if $(m/l)^{\frac{1}{2}}$ is equal to a root of $J_0(z)=0$.

(i) A pure imaginary root $z=iy$ of (2) is a real zero of

$$(ly^2+m)I_0(y)+nyI_1(y) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Now $I_0(y)$ and $I_1(y)$ are both positive for real positive y, so the expression (4) is certainly always positive if $y>0$ and conditions (3) are satisfied. Thus (4) has no real positive zero, and since it is an even function it has no real negative

[1] *Journ. and Proc. Roy. Soc. N.S.W.*, 1940, *74*, 342. This paper will be referred to as I.

[2] *Proc. Cambridge Phil. Soc.*, 1939, *35*, 394. *Proc. London Math. Soc.*, 1940, *46*, 361. These papers will be referred to as II and III, respectively.

[3] This is I (13).

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zero. If the conditions (3) are not satisfied there may be no, one, or two real positive zeros of (4).

(ii) The equation (2) has no complex roots if the conditions (3) are satisfied. For if ξ and η be conjugate complex roots of (2), we have

$$(l\xi^2-m)J_0(\xi)-n\xi J'_0(\xi)=0$$
$$(l\eta^2-m)J_0(\eta)-n\eta J'_0(\eta)=0.$$

Thus

$$l(\eta^2-\xi^2)J_0(\xi)J_0(\eta)+n\{\xi J'_0(\xi)J_0(\eta)-\eta J'_0(\eta)J_0(\xi)\}=0.$$

Therefore[4]

$$l(\eta^2-\xi^2)J_0(\xi)J_0(\eta)+n(\eta^2-\xi^2)\int_0^1 xJ_0(\xi x)J_0(\eta x)dx=0.$$

If $l\geqslant 0$, $n>0$ this is impossible, so there can be no complex root.

(iii) The equation (2) has no repeated roots, except possibly $z=0$, if the conditions (3) are satisfied. For writing[5]

$$y=(lz^2-m)J_0(z)+nzJ_1(z),$$

we find

$$yJ_1(z)+\frac{dy}{dz}J_0(z)=z\{(2l+n)J_0^2(z)+nJ_1^2(z)\}.$$

Thus if $z\neq 0$, $l\geqslant 0$, $n>0$, y and $\dfrac{dy}{dz}$ cannot vanish simultaneously.

3. *The expression*[6]

$$(lz^2+m)K_0(z)-nzK_1(z) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

has no zeros for $\mathrm{R}(z)\geqslant 0$, *provided*

$$l\geqslant 0,\ m\geqslant 0,\ n<0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

As in §2 we take $l\geqslant 0$, and if $l=0$, $m>0$. If $l=m=0$ the result is well known. If $n=0$, $l>0$, $m>0$ there are zeros at $\pm i(m/l)^{\frac{1}{2}}$.

(i) The expression (5) has no zeros for real positive z if the conditions (6) are satisfied, since $K_0(z)>0$, $K_1(z)>0$, for real positive z.

(ii) The expression (5) has no complex zero ξ. For if η is the conjugate of ξ, using the argument of §2 (ii) with G. and M., p. 70 (30), we have

$$(\xi^2-\eta^2)lK_0(\xi)K_0(\eta)-n(\xi^2-\eta^2)\int_1^\infty xK_0(\xi x)K_0(\eta x)dx=0,$$

and if $l\geqslant 0$, $n<0$ we have a contradiction.

(iii) The expression (5) has no pure imaginary zero $z=iy$, for this implies

$$(ly^2-m)[J_0(y)-iY_0(y)]-ny[J'_0(y)-iY'_0(y)]=0.$$

It follows that

$$J_0(y)Y'_0(y)-Y_0(y)J'_0(y)=0,$$

but this is equal to $(2/\pi y)$ and so we have a contradiction.

4. *The Zeros of*[7]

$$F(z)=[(lz^2-m)J_0(az)+nzJ_1(az)][(l'z^2-m')Y_0(bz)+n'zY_1(bz)]$$
$$-[(l'z^2-m')J_0(bz)+n'zJ_1(bz)][(lz^2-m)Y_0(az)+nzY_1(az)] \quad \ldots. \quad (7)$$

are all real and simple (except possibly for $z=0$), *provided*

$$l\geqslant 0,\ l'\geqslant 0,\ m\geqslant 0,\ m'\geqslant 0,\ n<0,\ n'>0 \quad \ldots\ldots\ldots\ldots \quad (8)$$

---

[4] Using Gray and Mathews, *Treatise on Bessel Functions*, p. 69 (23). This work will be referred to as G. and M.

[5] I am indebted to a referee for this argument.

[6] This result is needed in I, §§5 and 6.

[7] This is I (30).

We suppose $b>a$ in the discussion. The cases in which n or n' vanish are discussed in (iv) below.

(i) A pure imaginary zero $z=\pm iy$ of (7) is a real positive zero of

$$[(ly^2+m)I_0(ay)+nyI_1(ay)][(l'y^2+m')K_0(by)-n'yK_1(by)]$$
$$-[(l'y^2+m')I_0(by)+n'yI_1(by)][(ly^2+m)K_0(ay)-nyK_1(ay)]=0 \quad .. \quad (9)$$

which may be written

$$\begin{aligned}&(ly^2+m)(l'y^2+m')[I_0(ay)K_0(by)-K_0(ay)I_0(by)]\\&-nn'y^2[I_1(ay)K_1(by)-K_1(ay)I_1(by)]\\&+ny(l'y^2+m')[I_1(ay)K_0(by)+K_1(ay)I_0(by)]\\&-n'y(ly^2+m)[I_0(ay)K_1(by)+I_1(by)K_0(ay)] \quad \ldots\ldots\ldots\ldots\ldots \quad (10)\end{aligned}$$

It is known that $I_n(ay)K_n(by)-I_n(by)K_n(ay)$, $n=0$ and 1, have no real positive zeros. Taking $b>a$, it follows from the asymptotic expansions that they are negative for real positive y. Also $I_0(x)$, $I_1(x)$, $K_0(x)$, $K_1(x)$ are all positive for real positive x. Thus if the conditions (8) are satisfied, all four terms of (10) are $\leqslant 0$ for real positive y and thus there is no real positive zero of (9).

(ii) Suppose α is a zero of (7), then

$$U=[(l\alpha^2-m)Y_0(a\alpha)+n\alpha Y_1(a\alpha)]J_0(\alpha r)-[(l\alpha^2-m)J_0(a\alpha)+n\alpha J_1(a\alpha)]Y_0(\alpha r)$$

is a non-zero solution of the differential equation

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dU}{dr}\right)+\alpha^2U=0, \quad a<r<b \quad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

with boundary conditions

$$\left.\begin{aligned}(l\alpha^2-m)U-n\frac{dU}{dr}&=0, \quad r=a\\(l'\alpha^2-m')U-n'\frac{dU}{dr}&=0, \quad r=b\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (12)$$

Also, for any β,

$$V=[(l\beta^2-m)Y_0(a\beta)+n\beta Y_1(a\beta)]J_0(\beta r)-[(l\beta^2-m)J_0(a\beta)+n\beta J_1(a\beta)]Y_0(\beta r)$$

satisfies

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dV}{dr}\right)+\beta^2V=0, \quad a<r<b \quad \ldots\ldots\ldots\ldots\ldots \quad (13)$$

with

$$(l\beta^2-m)V-n\frac{dV}{dr}=0, \quad r=a \quad \ldots\ldots\ldots\ldots\ldots \quad (14)$$

From (11) and (13) it follows that

$$(\alpha^2-\beta^2)\int_a^b rUV\,dr+\left[rV\frac{dU}{dr}-rU\frac{dV}{dr}\right]_a^b=0,$$

and hence, using (12), (14) and the notation (7), we have

$$(\alpha^2-\beta^2)\left\{\int_a^b rUV\,dr+\frac{bl'}{n'}[UV]_{r=b}-\frac{al}{n}[UV]_{r=a}\right\}=\frac{b}{n'}F(\beta)[U]_{r=b}$$
$$\ldots\ldots\ldots\ldots \quad (15)$$

Suppose α is a complex zero of (7) and β its conjugate. Then $F(\beta)=0$, and (15) becomes

$$(\alpha^2-\beta^2)\left\{\int_a^b r\mid U\mid^2dr+\frac{bl'}{n'}\mid U\mid^2_{r=b}-\frac{al}{n}\mid U\mid^2_{r=a}\right\}=0.$$

Thus if $l\geqslant 0$, $l'\geqslant 0$, $n<0$, $n'>0$ we have a contradiction, and no complex root is possible.

(iii) To show that (7) has no repeated zeros, let α be a zero (real) of (7) and let β be real and tend to α. Then as $\beta\to\alpha$, $V\to U$ and $F(\beta)/(\beta-\alpha)\to F'(\alpha)$.

Thus (15) gives

$$2\alpha\left\{\int_a^b rU^2dr+\frac{bl'}{n'}[U^2]_{r=b}-\frac{al}{n}[U^2]_{r=a}\right\}=-\frac{b}{n'}F'(\alpha)[U]_{r=b}$$

If α is a repeated zero of (7), $F'(\alpha)=0$. Thus if $\alpha\neq 0$, and the conditions (8) are satisfied, we have a contradiction.

(iv) If $n=0$, $l'\geqslant 0$, $m'\geqslant 0$, $n'>0$ we have

$$F(z)=(lz^2-m)G(z),$$

where

$$G(z)=J_0(az)[(l'z^2-m')Y_0(bz)+n'zY_1(bz)] -Y_0(az)[(l'z^2-m')J_0(bz)+n'zJ_1(bz)].$$

The method of (ii) and (iii) may be used to show that the zeros of $G(z)$ are all real and simple. If $(m/l)^{\frac{1}{2}}$ is equal to a zero of $G(z)$, $F(z)$ will have double zeros at $\pm(m/l)^{\frac{1}{2}}$. A similar result holds for the case $n'=0$, $l\geqslant 0$, $m\geqslant 0$, $n<0$. If $n=n'=0$, we have

$$F(z)=(lz^2-m)(l'z^2-m')C_0(az,\ bz)$$

where $$C_0(az,\ bz)=J_0(az)Y_0(bz)-Y_0(az)J_0(bz).$$

The zeros of $C_0(az,\ bz)$ are known to be all real and simple. $F(z)$ has a repeated zero if $(m/l)^{\frac{1}{2}}$ or $(m'/l')^{\frac{1}{2}}$ coincides with one of them.

5. The method of solution used in I consisted of forming from the original differential equation and boundary conditions a subsidiary equation and boundary conditions, from the solution $\bar{v}(p)$ of which the solution $v(t)$ of the original problem was derived formally by the use of the inversion theorem, namely

$$v(t)=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}e^{\lambda t}\bar{v}(\lambda)d\lambda, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

and the solution was obtained in its final form from the line integral in (16) by using the contour of Fig. 1 or Fig. 2. To make the solutions rigorous we

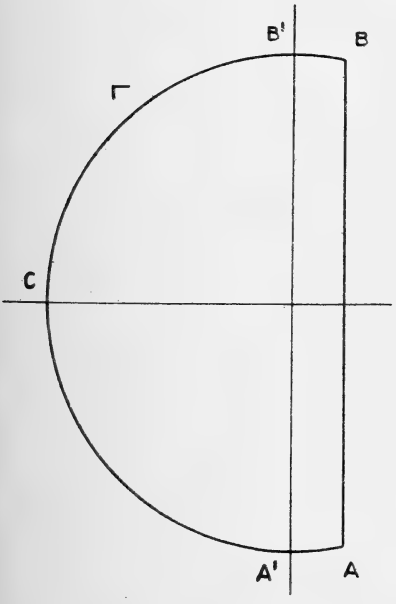


Fig. 1.

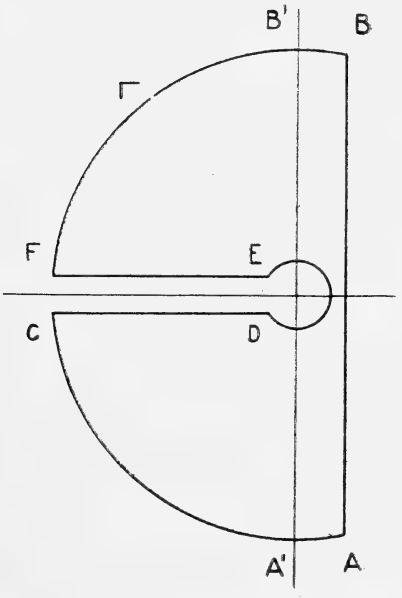


Fig. 2.

verify (*a*) that $v(t)$ given by (16) satisfies the conditions of the problem, and (*b*) that the integrals over the large circles of Figs. 1 and 2 tend to zero as the radius tends to infinity.

6. The method of verifying that solutions obtained in the form (16) satisfy their differential equations and initial and boundary conditions consists of transforming the path L, $(\gamma - i\infty, \gamma + i\infty)$, of (16) into a path L' which begins at infinity in the direction $\arg\lambda = -\beta$, $\pi > \beta > \frac{1}{2}\pi$, keeps all singularities of the integrand to the left and ends in the direction $\arg\lambda = \beta$. The verification is then performed on the integrals over L'. Most of the verification is performed by the use of Theorem 2 of II, which is restated here for convenience and to include two small extensions proved as in II.

THEOREM 2. *If* $f(\lambda, \xi)$ *is an analytic function of* λ *on and to the right of the path* L', *and if*

$$|f(\lambda, \xi)| < CR^k \exp[-\xi R^{\frac{1}{2}} \cos \tfrac{1}{2}\theta],$$

when $\lambda = \mathrm{Re}^{\pm i\theta}$, $\pi > \theta_0 \geqslant \theta \geqslant 0$, $R > R_0$, *where* C, $k < 1$, R_0, *and* $\theta_0 > \frac{1}{2}\pi$ *are constants, then*

(i) $$\int_L e^{\lambda t} f(\lambda, \xi) \frac{d\lambda}{\lambda} = \int_{L'} e^{\lambda t} f(\lambda, \xi) \frac{d\lambda}{\lambda},$$

provided that either $t \geqslant 0$, $\xi > 0$, *or* $t > 0$, $\xi \geqslant 0$.

(ii) $$\int_{L'} e^{\lambda t} f(\lambda, \xi) \frac{d\lambda}{\lambda}$$

is uniformly convergent with respect to t *in* $t \geqslant 0$ *for fixed* $\xi > 0$, *and with respect to* ξ *in* $\xi \geqslant 0$ *for fixed* $t > 0$. *Also the integral may be differentiated under the integral sign with respect to* t *in* $t \geqslant 0$ *for fixed* $\xi > 0$, *or in* $t \geqslant t_0 > 0$ *for fixed* $\xi \geqslant 0$, *and the resulting integral is uniformly convergent with respect to* ξ *in* $\xi \geqslant 0$, *for fixed* $t > 0$.

(iii) $$\lim_{t \to o} \int_{L'} e^{\lambda t} f(\lambda, \xi) \frac{d\lambda}{\lambda} = 0, \text{ for fixed } \xi > 0.$$

(iv) *If, in addition,* $\partial f/\partial \xi$ *and* $\partial^2 f/\partial \xi^2$ *satisfy conditions of the type satisfied by* $f(\lambda, \xi)$ *except that* k *need not be less than* 1, *then*

$$\int_{L'} e^{\lambda t} f(\lambda, \xi) \frac{d\lambda}{\lambda}$$

may be differentiated twice under the integral sign with respect to ξ, *in* $\xi \geqslant 0$, *for fixed* $t > 0$.

(v) *If the range of* ξ *extends to infinity,*

$$\lim_{\xi \to \infty} \int_{L'} e^{\lambda t} f(\lambda, \xi) \frac{d\lambda}{\lambda} = 0,$$

for fixed $t \geqslant 0$.

Proof of (v) is as for the special case in Paper II.

In §§7, 8, 9 verifications of the solutions of §§2 and 5 of I and the source problem of I, §3 are given in detail. The results of I, §4 and the other source problems of I may be treated in the same way.

7. *Verification that I* (11) *satisfies the conditions of I*, §2.

We write $f(\lambda)=(k_1\lambda+k_3)I_0(\mu a)+k_2\mu I_1(\mu a)$ ..... (17)
where $\mu=\sqrt{(\lambda/\varkappa)}$.

From the asymptotic expansions of the Bessel functions it follows that when $\lambda=\varkappa\rho e^{i\theta}$, $\pi>\theta_0\geqslant\theta\geqslant 0$ ..... (18)

$$|f(\lambda)|>C\rho^{\alpha}\exp[a\rho^{\frac{1}{2}}\cos\tfrac{1}{2}\theta],\text{ if }\rho>\rho_0 \quad\ldots\ldots (19)$$

where[8] α is 3/4, 1/4, or $-1/4$ according as $k_1\neq 0$; $k_1=0$, $k_2\neq 0$; or $k_1=k_2=0$; respectively.

Also since $|I_0(z)|\leqslant\exp|R(z)|$ ..... (20)
we have, when λ has the value (18),

$$|I_0(\mu r)|<C\exp[r\rho^{\frac{1}{2}}\cos\tfrac{1}{2}\theta].$$

$$\text{Thus }\left|\frac{I_0(\mu r)}{f(\lambda)}\right|<C\rho^{-\alpha}\exp[-(a-r)\rho^{\frac{1}{2}}\cos\tfrac{1}{2}\theta],\ \rho>\rho_0,\ 0\leqslant r\leqslant a \quad\ldots\ldots (21)$$

where α has the values 3/4, 1/4 or $-1/4$.

The derivatives with respect to r of the left-hand side of (21) satisfy similar inequalities. Thus for all values of the k the integrand of I (11) satisfies the conditions of Theorem 2 (these are taken, here and subsequently, to include those of Theorem 2 (iv)). It follows immediately from the Theorem that

$$v=\frac{k_4}{2\pi i}\int_{L'}\frac{e^{\lambda t}I_0(\mu r)d\lambda}{\lambda f(\lambda)},\text{ when } t\geqslant 0,\ 0\leqslant r<a \quad\ldots\ldots (22)$$

$$\text{or } t>0,\ 0\leqslant r\leqslant a,$$

that $\lim_{t\to o} v=0$, for fixed r in $0\leqslant r<a$, and that v satisfies its differential equation.

To verify the boundary condition I (4) we take v in the form (22) and observe that by Theorem 2 (ii) we may differentiate under the integral sign with respect to r in $0\leqslant r\leqslant a$ for fixed $t>0$, and with respect to t in $t\geqslant t_0>0$ for fixed r in $0\leqslant r\leqslant a$. Thus

$$k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3 v=\frac{k_4}{2\pi i}\int_{L'}\frac{e^{\lambda t}\{k_1\lambda+k_3)I_0(\mu r)+k_2\mu I_1(\mu r)\}d\lambda}{\lambda f(\lambda)}$$

and by (ii) and (iv) of Theorem 2 this integral is uniformly convergent with respect to r in $0\leqslant r\leqslant a$ for fixed $t>0$. Thus

$$\lim_{r\to a}\left(k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3 v\right)=\frac{k_4}{2\pi i}\int_{L'}\frac{e^{\lambda t}d\lambda}{\lambda}=k_4.$$

8. *Verification that I* (36) *satisfies the conditions of I*, §5.

Writing $g(\lambda)=(k_1\lambda+k_3)K_0(\mu a)-k_2\mu K_1(\mu a)$ ..... (23)
we find as in §7 that for $\lambda=\varkappa\rho e^{i\theta}$, $\pi\geqslant\theta\geqslant 0$,

$$\left|\frac{K_0(\mu r)}{g(\lambda)}\right|<C\rho^{\alpha}\exp[-(r-a)\rho^{\frac{1}{2}}\cos\tfrac{1}{2}\theta],\ \rho>\rho_0 \quad\ldots\ldots (24)$$

where $\alpha=-1$, $-\frac{1}{2}$, or 0 according as $k_1\neq 0$; $k_1=0$, $k_2\neq 0$; or $k_1=k_2=0$, respectively. The derivatives satisfy similar conditions.

Thus in all cases the conditions of Theorem 2 are satisfied and it follows that the path can be deformed into L', that v satisfies the differential equation, and that $\lim_{t\to o} v=0$. It is verified as in §7 that the boundary condition at

[8] C is used for any positive constant, ρ_0, ρ_1, . . . for fixed values of ρ, etc.

$r=a$ is satisfied. The remaining condition

$$\lim_{r\to\infty} v=0$$

follows from Theorem 2 (v).

9. *Verification of the solution for an instantaneous cylindrical surface source over* $\mathrm{r}=\mathrm{r}'$ *in the solid cylinder* $0\leqslant \mathrm{r} < \mathrm{a}$.

From the results of I, §3, with the notation (17) and (23) we have

$$v=-\frac{Q}{4\pi^2 i\varkappa}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{I_0(\mu r')\{I_0(\mu r)g(\lambda)-K_0(\mu r)f(\lambda)\}e^{\lambda t}d\lambda}{f(\lambda)},\quad r'\leqslant r<a \qquad \ldots\ldots\ldots\ldots\ldots\ldots(27)$$

and

$$w=-\frac{Q}{4\pi^2 i\varkappa}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{I_0(\mu r')I_0(\mu r)g(\lambda)e^{\lambda t}d\lambda}{f(\lambda)},\quad 0\leqslant r<a \qquad \ldots\ldots\ldots\ldots(28)$$

We have to verify that v satisfies I (16) and that w satisfies I (19) and I (20).

When $\lambda=\varkappa\rho e^{i\theta}$, $\pi>\theta_0\geqslant\theta\geqslant 0$,

$$\left|\frac{I_0(\mu r')I_0(\mu r)g(\lambda)}{f(\lambda)}\right|<C\rho^{-\frac{1}{2}}\exp[(r+r'-2a)\rho^{\frac{1}{2}}\cos\tfrac{1}{2}\theta],\quad \rho>\rho_0 \ldots\ldots(29)$$

$$\left|\frac{I_0(\mu r')\{I_0(\mu r)g(\lambda)-K_0(\mu r)f(\lambda)\}}{f(\lambda)}\right|<C\rho^{-\frac{1}{2}}\exp[(r'-r)\rho^{\frac{1}{2}}\cos\tfrac{1}{2}\theta],\quad r'\leqslant r\leqslant a,\ \rho>\rho_1\ldots\ldots\ldots\ldots(30)$$

with similar results for the derivatives.

It follows from (29) and Theorem 2 that w satisfies I (19) and I (20). Also, it follows from (30) that the path of integration in (27) may be deformed into L', and that the integral over L' may be differentiated under the integral sign with respect to r in $r'<r\leqslant a$ for fixed $t>0$, and with respect to t in $t\geqslant t_0>0$ for fixed r in $r'<r\leqslant a$. Thus

$$k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3 v=-\frac{Q}{4\pi^2 i\varkappa}\int_{L'}\frac{\varphi(\lambda,\ r)e^{\lambda t}}{f(\lambda)}d\lambda,$$

where $\varphi(\lambda,\ r)=I_0(\mu r')\{[(k_1\lambda+k_3)I_0(\mu r)+k_2\mu I_1(\mu r)]g(\lambda)$
$-[(k_1\lambda+k_3)K_0(\mu r)-k_2\mu K_1(\mu r)]f(\lambda)\}$

and the integral is uniformly convergent with respect to r in $r'<r\leqslant a$ for fixed $t>0$. Therefore

$$\lim_{r\to a}\left(k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3 v\right)=0.$$

Since we have used the inversion theorem purely formally, and not established conditions for its validity, to complete the proof it is necessary to show that the application of the inversion theorem to I (21) gives I (18).

We consider the region $0\leqslant r\leqslant r'$. Applying the inversion theorem to I (21) gives

$$\frac{Q}{4\pi^2 i\varkappa}\int_{\gamma-i\infty}^{\gamma+i\infty}I_0(\mu r)K_0(\mu r')e^{\lambda t}d\lambda$$

Now on $\lambda=\varkappa\rho e^{i\theta}$

$|\,I_0(\mu r)K_0(\mu r')\,|<C\rho^{-\frac{1}{2}}\exp[-(r'-r)\rho^{\frac{1}{2}}\cos\tfrac{1}{2}\theta],\ 0\leqslant r\leqslant r',\ \rho>\rho_0$.

Thus by II, Theorem 1 (footnote), the integrals over the arcs $BB'F$ and $AA'C$ of Fig. 2, tend to zero as $\rho\to\infty$ for $t>0$, $0\leqslant r\leqslant r'$.

Therefore

$$\frac{Q}{4\pi^2 i\varkappa}\int_{\gamma-i\infty}^{\gamma+i\infty} I_0(\mu r)K_0(\mu r')e^{\lambda t}d\lambda$$

$$=-\frac{2\varkappa Q}{4\pi^2 i\varkappa}\int_0^\infty e^{-\varkappa u^2 t}uJ_0(ur)[K_0(iur')-K_0(-iur')]du$$

$$=\frac{Q}{2\pi}\int_0^\infty e^{-\varkappa u^2 t}J_0(ur)J_0(ur')udu$$

$$=\frac{Q}{4\pi\varkappa t}\exp\left(-\frac{r'+r'^2}{4\varkappa t}\right)I_0\left(\frac{rr'}{2\varkappa t}\right),\ t>0,\ 0\leqslant r\leqslant r'.$$

The proof for the other range is similar.

10. It remains to show that for the problems of I the integrals round the arcs $BB'C$ and $AA'C$ of the circle $\ulcorner$ of I, Fig. 1, or $BB'F$ and $AA'C$ of I, Fig. 2, tend to zero as the radii tend to infinity. When Fig. 1 is used the radius is to tend to infinity through a sequence of values avoiding the poles of the integrand; these poles have been discussed in §§2, 3, 4. In all cases we show that the integrands of the line integrals for v satisfy the conditions of II, Theorem 1, and the result follows. The problems of I, §§2, 3, 5, are discussed in §§12, 13, 14; the remaining problems are treated in the same way.

11. *Lemma.* *For* $\lambda=\varkappa(n+\frac{1}{2})^2\frac{\pi^2}{a^2}e^{i\theta}$, $\mu=\sqrt{(\lambda/\varkappa)}$, $\pi\geqslant\theta\geqslant 0$.

$$\left|\cosh\left(\mu a-\frac{1}{4}\pi i\right)\right|>C\exp[(n+\tfrac{1}{2})\pi\cos\tfrac{1}{2}\theta]\quad\ldots\ldots\ldots\ldots\quad(31)$$

where C is a constant independent of n.

$$\left|\cosh\left(\mu a-\frac{1}{4}\pi i\right)\right|^2=\left|\cosh\left[(n+\tfrac{1}{2})\pi e^{i\theta/2}-\frac{1}{4}\pi i\right]\right|^2$$

$$=\tfrac{1}{2}\left\{\cosh[(2n+1)\pi\cos\tfrac{1}{2}\theta]+\cos\left[(2n+1)\pi\sin\tfrac{1}{2}\theta-\frac{\pi}{2}\right]\right\}$$

$$=\tfrac{1}{2}\cosh[(2n+1)\pi\cos\tfrac{1}{2}\theta]\{1+\sin[(2n+1)\pi\sin\tfrac{1}{2}\theta]\operatorname{sech}[(2n+1)\pi\cos\tfrac{1}{2}\theta]\}$$

Now let $\beta=2\sin^{-1}\dfrac{2n+3/4}{2n+1}$.

Then $0\leqslant\sin[(2n+1)\pi\sin\tfrac{1}{2}\theta]\operatorname{sech}[(2n+1)\pi\cos\tfrac{1}{2}\theta]<2^{-\frac{1}{2}}$, when $\pi\geqslant\theta\geqslant\beta$.

Also, when $\beta\geqslant\theta\geqslant 0$,

$|\sin[(2n+1)\pi\sin\tfrac{1}{2}\theta]\operatorname{sech}[(2n+1)\pi\cos\tfrac{1}{2}\theta]|<\operatorname{sech}[(2n+1)\pi\cos\tfrac{1}{2}\beta]<C<1$

Thus, when $\pi\geqslant\theta\geqslant 0$,

$$\left|\cosh\left(\mu a-\frac{1}{4}\pi i\right)\right|>C\exp[(n+\tfrac{1}{2})\pi\cos\tfrac{1}{2}\theta]$$

The same argument gives, when $\lambda=\varkappa(n+\frac{1}{2})^2\frac{\pi^2}{a^2}e^{i\theta}$,

$$\left|\cosh\left(\mu a-\frac{3}{4}\pi i\right)\right|>C\exp[(n+\tfrac{1}{2})\pi\cos\tfrac{1}{2}\theta]\quad\ldots\ldots\quad(32)$$

12. *The problem of I*, §2.

Here, using the notation (17)

$$v=\frac{k_4}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{e^{\lambda t}I_0(\mu r)d\lambda}{\lambda f(\lambda)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (33)$$

Now it follows from the asymptotic expansions of the Bessel functions that

$$f(\lambda)=\frac{2(k_1\lambda+k_3)e^{\frac{1}{4}\pi i}}{(2\pi\mu a)^{\frac{1}{2}}}\cosh\left(\mu a-\frac{1}{4}\pi i\right)+\frac{2k_2\mu e^{\frac{1}{4}\pi i}}{(2\pi\mu a)^{\frac{1}{2}}}\cosh\left(\mu a-\frac{3}{4}\pi i\right)$$

$$+\text{similar terms } 0\left(\frac{1}{\mu}\right) \text{ compared with the above.}$$

Thus,[9] if $\lambda=\varkappa(n+\frac{1}{2})^2\frac{\pi^2}{a^2}e^{i\theta}$, $\pi\geqslant\theta>0$

$$\left|f(\lambda)\right|>Cn^\alpha\exp[(n+\tfrac{1}{2})\pi\cos\tfrac{1}{2}\theta),\ n>n_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (34)$$

where the results (31) and (32) have been used and α is $3/2$, $\frac{1}{2}$ or $-\frac{1}{2}$ according as $k_1\neq0$; $k_1=0$, $k_2\neq0$; or $k_1=k_2=0$.

Also $|I_0(z)|\leqslant\exp|R(z)|$.

Thus on $\lambda=\varkappa(n+\frac{1}{2})^2\frac{\pi^2}{a^2}e^{i\theta}$

$$\left|\frac{I_0(\mu r)}{f(\lambda)}\right|<Cn^\alpha\exp\left\{(n+\tfrac{1}{2})\pi\,.\,\frac{(r-a)}{a}\cos\tfrac{1}{2}\theta\right\},\ \pi\geqslant\theta\geqslant0,\ 0\leqslant r\leqslant a,\ n>n_3$$

where α is $-3/2$, $-\frac{1}{2}$ or $\frac{1}{2}$ according as $k_1\neq0$; $k_1=0$, $k_2\neq0$; or $k_1=k_2=0$.

In all cases the conditions of II, Theorem 1, are satisfied and thus the integral over Γ tends to zero as its radius tends to infinity if

either $0\leqslant r\leqslant a$, $t>0$

or $0\leqslant r<a$, $t\geqslant0$.

13. *The source problem of I*, §3.

Here, in the notation (16),

$$v=-\frac{Q}{4\pi^2i\varkappa}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{I_0(\mu r')\{I_0(\mu r)g(\lambda)-K_0(\mu r)f(\lambda)\}e^{\lambda t}d\lambda}{f(\lambda)},\ r'\leqslant r<a.$$

From the asymptotic expansions it follows that, for

$$\lambda=\varkappa(n+\tfrac{1}{2})^2\frac{\pi^2}{a^2}e^{i\theta},\ \pi\geqslant\theta\geqslant0$$

$$|I_0(\mu r')\{I_0(\mu r)g(\lambda)-K_0(\mu r)f(\lambda)\}|<Cn^\alpha\exp\left((n+\tfrac{1}{2})\pi\frac{(r'-r+a)}{a}\cos\tfrac{1}{2}\theta\right),$$

$$r'\leqslant r<a,\ n>n_1$$

where $\alpha=\frac{1}{2}$, $-\frac{1}{2}$, $-3/2$ according as $k_1\neq0$; $k_1=0$, $k_2\neq0$; $k_1=k_2=0$.

Thus, using (34), we have when

$$\lambda=\varkappa(n+\tfrac{1}{2})^2\frac{\pi^2}{a^2}e^{i\theta},\ \pi\geqslant\theta\geqslant0$$

$$\left|\frac{I_0(\mu r')\{I_0(\mu r)g(\lambda)-K_0(\mu r)f(\lambda)\}}{f(\lambda)}\right|<\frac{C}{n}\exp\left\{(n+\tfrac{1}{2})\pi\frac{(r-r')}{a}\cos\tfrac{1}{2}\theta\right\}$$

$$r'\leqslant r<a,\ n>n_2.$$

Thus the conditions of II, Theorem 1, are satisfied for $t>0$ if $r'\leqslant r\leqslant a$, and similarly they are satisfied if $0\leqslant r\leqslant r'$.

---

[9] These circles do not pass through any pole of the integrand of (33).

14. *The problem of I*, §5.

Here in the notation (23)

$$v=\frac{k_4}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{e^{\lambda t}K_0(\mu r)d\lambda}{\lambda g(\lambda)}$$

and since the order property (24) holds in $\pi\geqslant\theta\geqslant 0$ the conditions of II, Theorem 1, are satisfied.

The University of Tasmania.

THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

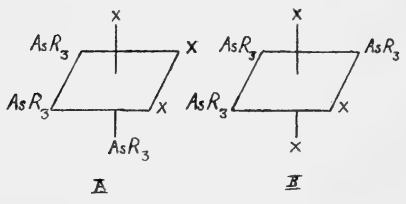
Part III. Compounds of Rhodic Halides with Tertiary Arsines.

By F. P. Dwyer, M.Sc.,
and R. S. Nyholm, B.Sc.

(*Manuscript received, October 15, 1941. Read, November 5, 1941.*)

In a previous communication (This Journal, LXXV, p. 127), the preparation of a number of rhodous halides stabilised with diphenylmethylarsine was described. In all of these compounds the central metallic atom showed a coordination number of six achieved by bridging. Since it appeared probable that the compounds resulted by the reduction of the arsine coordinated rhodic halides, and not by reduction of the simple rhodic halides to the lower valency state followed by addition of the arsine, it was considered useful to investigate the coordination compounds with rhodic halides and various tertiary arsines, in order to determine the possibility of preparing rhodous compounds with the lower coordination number of four, as well as to contrast the stability and reactions of rhodium in both valency states.

By working with diphenylmethylarsine, and dimethyl-p-tolylarsine it was found that compounds of only one type could be obtained, viz. $RhX_3 . 3AsR_3$, where X=Cl, Br, or I. If the usual, well established, octahedral distribution of the bonds about hexacovalent rhodium is assumed, substances of this formula are capable of existence in two isomeric forms (A), (B).



Two forms of many of the rhodic compounds were actually isolated, but showed large differences in melting point and solubilities, and were obtained under widely different experimental conditions. Although not necessarily the case, isomeric forms of the type (A) and (B) might be expected to exhibit very similar properties and reactions.

The lower melting compound form II was extremely soluble in organic solvents such as benzene and chloroform, and even on boiling with silver nitrate in acetone solution gave only a mere trace of the silver halide. (In this regard the iodides were anomalous.) The molecular weight was normal, and the lower melting form II must thus be considered the neutral complex $(Rh . X_3 . 3AsR_3)^\circ$.

The higher melting form I of the same empirical formula was only sparingly soluble in organic solvents, but dissolved on long contact or on boiling. When the solvent was removed, however, it was found to have passed completely to the lower melting form II. Thus the molecular weight (cryoscopic) in benzene, was identical with that of the lower melting form in the same solvent, and this latter substance alone was found when the solvent was removed in a rapid stream of air at 6° C. The higher melting form I gave an appreciable precipitate with silver nitrate in alcohol or acetone solution.

When tested for dimorphism by the method of Mellor (This Journal, 1937-38, *71*, 536), it was found that the lower melting form II could be recrystallised from

aqueous alcohol containing halogen acid, provided that the operations were performed rapidly. With this particular solvent alone, the higher melting form I was also crystallisable. Thus the two forms are not different crystals of the same chemical entity. Further, the solution of form I is darker than that of form II.

Finally, it was found that the higher melting form I tended to come down preferentially in solutions containing an excess of halogen acid, i.e. in which the rhodium was largely in the form of the complex ion $(RhX_6)'''$, and by refluxing the lower melting form II in aqueous alcoholic solution with excess of the acid or potassium halide, the higher melting form I was deposited quantitatively, provided that the alcohol concentration was not too high. It is suggested, therefore, that the high melting form I is possibly the electrolytic complex dimeride $(Rh(AsR_3)_6)\ (RhX_6)'''$. With the exception of the above observations of the effect of halide ions in effecting the transformation of form II to form I, the authors have not been able to find any crucial test for choosing between an isomerism based upon the two possible forms (A) and (B), or an interpretation based upon the complex dimeride shown above. In assessing the value of the effect noted with halide ions, it must also be pointed out that the actual form isolated (i.e. form I or form II) even in the presence of excess halide ion seems to depend on the relative solubilities of the two forms, since, whilst with diphenylmethylarsine all six forms of rhodic chloride, bromide, iodide, with the more soluble dimethyl-p-tolylarsine the higher melting form I could be isolated in the case of the iodide only.

The compounds isolated, as might be anticipated, with increase in the molecular weight of the halogen increased in melting point, and darkened in colour, but also became more reactive towards silver nitrate. Thus form II of the chloride was almost without reaction towards this reagent, the bromide gave a just perceptible precipitate, but the iodide instantly precipitated the whole of the halogen as silver iodide. This reaction does not necessarily suggest that the bonding in the iodide is weaker than in the chloride, since the effect may well be due to the lower solubility of silver iodide. The rhodic compounds were found to differ considerably from the rhodous compounds, previously described, as regards solubility, but most notably in their failure to reduce silver nitrate to the metal even in boiling acetone or pyridine solution.

Experimental.

Compounds with Rhodic Chloride.

(*a*) *Diphenylmethylarsine.*—To 10 mls. of rhodium trichloride solution containing 0·096 g. of rhodium were added 0·7 g. diphenylmethylarsine dissolved in alcohol (80 mls.) and concentrated hydrochloric acid (10 mls.). The mixture was refluxed until a precipitate came down (about 10 mins.), and then heated for a further 5 minutes.

The precipitated material was removed by filtration, washed many times with cold 60% alcohol, and dried at 100° C.: Form I.

The filtrate after the removal of the form I was precipitated with water, and after washing, and drying at room temperature, was crystallised from benzene and petroleum ether: Form II.

Form I.—This substance was obtained in orange rounded crystalline masses, m.p. 176–178° C. It was sparingly soluble in alcohol, acetone, benzene and chloroform, but dissolved by long contact or on boiling. The material recovered, after such dissolution, was found always to have undergone transformation to form II. The substance could be crystallised from alcohol containing a large excess of hydrochloric acid. On boiling with acetone and silver nitrate it gave a perceptible precipitate of silver chloride.

Found: Rh, 11·32%; Cl, 11·20%; mol. wt., in benzene cryoscopic, 898, in acetone ebullioscopic, 796. (In both molecular weight determinations the recovered material was entirely in the form II.)

Calculated for $(Rh(AsR_3)_6).(RhCl_6)$: Rh, 11·23%; Cl, 11·31%; mol. wt., 1884.

Form II.—This gave a lemon yellow microcrystalline powder, m.p. 122–124° C. It was extremely soluble in alcohol, acetone, benzene and chloroform. By boiling with alcohol containing a large excess of hydrochloric acid it was transformed into form I. No trace of silver chloride was precipitated by heating with acetone and silver nitrate.

Found: Rh, 11·26%; Cl, 11·1%; mol. wt. in benzene cryoscopic, 897.

Calculated for $(RhCl_3 . 3AsR_3)$: Rh, 11·23%; Cl, 11·31%; mol. wt., 942.

By varying the relative amounts of arsine and rhodium chloride over wide ranges no compounds other than the above could be isolated. Similarly, when either form I or II was refluxed with excess arsine or rhodium chloride in alcoholic solution they were recovered unchanged.

(*b*) *Dimethyl-p-tolylarsine.*—Operating with this arsine under the conditions above a slight precipitate only was obtained. This was identical with the larger amount of material obtained by the addition of water, and appeared to be form II entirely. After crystallisation from benzene and petroleum ether, the yellow microcrystalline powder melted at 86–88° C., and was extremely soluble in alcohol, acetone and benzene.

Found: Rh, 12·7%; calculated for $(RhCl_3 . 3AsR_3)$: Rh, 12·9%.

Repeated attempts to prepare the other form by boiling with aqueous alcohol and hydrochloric acid failed to yield any trace.

Compounds with Rhodic Bromide.

(*a*) *Diphenylmethylarsine.*—Rhodic bromide treated in alcoholic solution with the arsine (3 mols) and hydrobromic acid was refluxed until about half of the rhodium was precipitated. After removal of the precipitate (form I), the filtrate was precipitated with water to give form II.

Form I.—The bright red crystalline powder was very sparingly soluble in all solvents, and melted at 191° C. Treatment with silver nitrate and acetone precipitated about 20% of the halogen as silver bromide.

Found: Rh, 9·72%; calculated for $(Rh(AsR_3)_6)(RhBr_6)$: Rh, 9·57%.

Form II.—After recrystallisation from benzene and petroleum ether the orange red microcrystalline powder melted at 116° C. It was easily soluble in all organic solvents to deep red solutions.

Found: Rh, 9·40%; calculated for $(RhBr_3 . 3AsR_3)$: Rh, 9·57%.

(*b*) *Dimethyl-p-tolylarsine.*—Rhodic bromide treated with the arsine in the presence of hydrobromic acid as above gave no precipitate even on prolonged boiling. The red solution after precipitation with water gave only form II, m.p. 109° C., extremely soluble in alcohol, acetone and benzene. Attempts to prepare form I by boiling with aqueous alcohol and hydrobromic acid were fruitless.

Found: Rh, 10·98%; calculated for $(RhBr_3 . 3AsR_3)$: Rh, 11·05%.

Compounds with Rhodic Iodide.

(*a*) *Diphenylmethylarsine.*—Owing to the insolubility of rhodic iodide in water or alcohol, the preparative methods used for the chloride and bromide compounds could not be used and the two forms were prepared by different methods.

Form II.—Rhodium trichloride solution (10 mls.), containing 0·096 g. of rhodium, was treated with hydriodic acid solution 57% (20 mls.), alcohol (80 mls.), and diphenylmethylarsine (0·7 g.). The mixture was boiled until a faint precipitate commenced to form, filtered rapidly and cooled. The purplish red precipitate was washed several times with water, and finally with petroleum ether. The substance was extremely soluble in benzene and organic solvents, and was the covalent form. Treated with silver nitrate in acetone solution, the purplish red colour was instantly discharged and a precipitate of silver iodide thrown down.

Found: Rh, 8·59%; calculated for $(RhI_3 . 3AsR_3)$: Rh, 8·46%.

Form I.—Rhodium trichloride solution (10 mls.), containing 0·096 g. of rhodium was treated with alcohol (80 mls.) and the arsine (0·7 g.). The mixture was then warmed carefully until the arsine had dissolved completely, and potassium iodide (4 g.) dissolved in 10 mls. of hot water added. After refluxing for a few minutes, water was added until a precipitate commenced to form, and the refluxing continued, when a dense purplish red precipitate came down in large amount. The precipitate was washed with water and then with alcohol, in which it was completely insoluble. The substance formed twinned plates and needles, m.p. 200° C. Treated with acetone and silver nitrate, it precipitated the whole of the halogen instantly.

Found: Rh, 8·48%; calculated for $(Rh(AsR_3)_6(RhI_6)$: Rh, 8·46%.

(*b*) *Dimethyl-p-tolylarsine.—Form I.*—Prepared as above, this gave bright red plates and needles, m.p. 200° C.

Found: Rh, 9·60%; calculated for $(Rh(AsR_3)_6)(RHI_6)$: Rh, 9·75%.

Form II.—Prepared in a similar manner to the compound with diphenylmethylarsine, this gave a purplish red microcrystalline powder from petroleum ether and benzene. It melted at 85–86° C., and was extremely soluble in organic solvents.

Found: Rh, 9·74%; calculated for $(RhI_3 . 3AsR_3)$: Rh, 9·75%.

Summary.

The compounds of rhodic halides with tertiary arsines have been found to exist in two forms: one easily soluble in organic media, and the other probably a complex dimeride, only sparingly soluble in such media.

In all cases the compounds were found to possess the general formula $RhX_3 . 3AsR_3$, indicating a coordination number of six. They differ notably from the arsine coordination compounds with rhodous halides previously described in their failure to reduce silver nitrate to the metal.

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THE TRIASSIC FISHES OF NEW SOUTH WALES.

By R. T. Wade, M.A., Ph.D.

(With Plate VII and one Text-figure.)

(*Manuscript received, October 22, 1941. Read, November 5, 1941.*)

(1) Note on a "Flying Fish" from the Middle Triassic of Brookvale, N.S.W.

Genus (?) Thoracopterus

(Bronn, N. Jahrb, f. Min., 1858, p. 12.)

Material.—Two specimens, P.15793 in the British Museum, and U.S.G.D.151 in the Geological Museum, Sydney University.

Description.—The specimen in Sydney shows a large part of a pectoral fin, which is 7·4 cm. long and includes not less than fifteen fin-rays. Distally these branch repeatedly, yielding six to eight fine rays each. In the other specimen the fin-rays are very long, rounded, divided into long segments, and branch distally. A few narrow, elongated, smooth scales are also preserved.

Remarks.—*Cephaloxenus*, *Dollopterus*, *Gigantopterus* and *Thoracopterus* are Triassic fishes with such large pectoral fins that they have been thought to be "flying fishes". From the scanty material here, it is, of course, impossible to determine the relationship of the specimens, and they are referred to *Thoracopterus* for convenience of record only.

(2) Corunegenys bowralensis, a New Semionotid Fish from the Triassic of Bowral, N.S.W.

Sub-Class NEOPTERYGII.

Order Holostei.

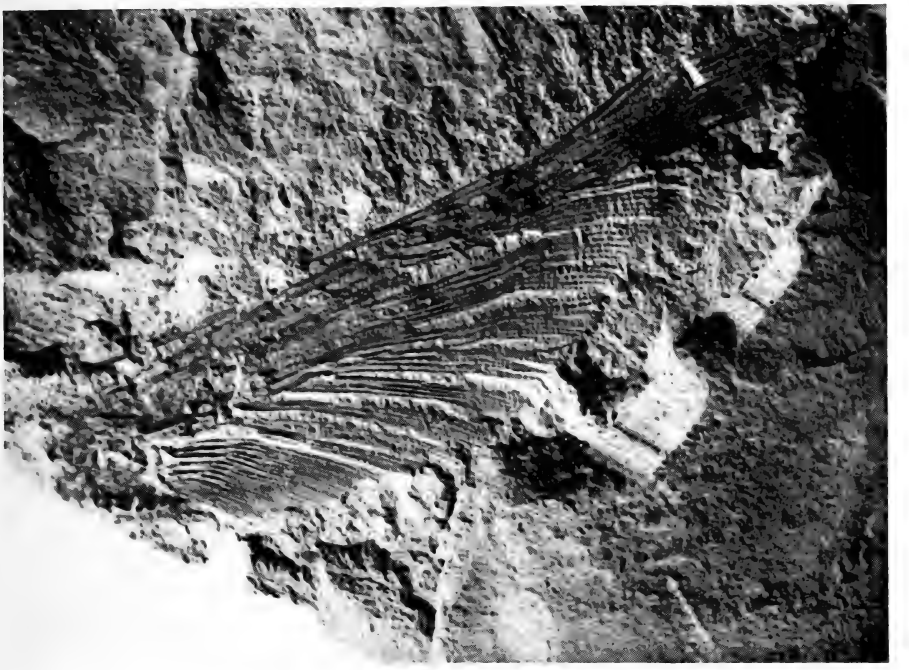
Family **Semionotidæ.**

Genus Corunegenys nov.

Diagnosis.—Small Semionotidæ with fusiform bodies, deepened anterior to dorsal fin; dorsal margin descending rapidly from just behind back of head to snout. Eyes comparatively large, suspensorium not greatly inclined forwards: mouth of moderate size. Quadrate articulation well back; quadrate angle obtuse. Tabulars triangular, wide, bordering both parietals and supratemporals. Paired parietals small, nearly square. Supratemporals moderately wide, irregularly shaped. Frontals long, widest behind orbits. Nasals larger, longer than wide. Operculum large, deeper than long. Suboperculum much smaller than operculum. Interoperculum small, triangular, well below suboperculum. Median gular large. Maxilla small, tapering, slightly concave at oral margin. Mandible long, deep at coronoid area, tapering anteriorly. Hinder end of supra-orbital sensory canals in parietals.

Post-temporals triangular. Supracleithra deep, triangular, slightly expanded at upper end. Cleithra of type normal to family.

Dermal fin-rays few, well spaced, with long, tapering proximal shafts and distal division into small joints; in caudal fin long proximal joints present only in middle rays; fulcra few; rays of paired fins slender.



Tail abbreviate-heterocercal, not deeply cleft.

Scales thick, smooth, rhombic, with entire margins; flank scales much deeper than long; ventral scales longer than deep.

Genotype.—*C. bowralensis.*

Remarks.—Among the Semionotidæ it is most like *S. capensis* in the structure of the head; but it cannot be assigned to that genus because of the absence of a circumorbital ring consisting of numerous bones, its more nearly vertical suspensorium, and its longer maxilla.

Its name is derived from Gr. corune, a club and genus, jaw, in allusion to the club-like appearance of the tapering lower jaw and maxilla.

Corunegenys bowralensis, sp. nov.

Diagnosis.—As for genus, with the following additions: the dorsal fin, which arises slightly behind the middle point of the dorsal margin, comprises about thirteen rays; the anal fin, placed entirely behind the dorsal, includes about ten rays; the caudal fin has some twenty-three rays.

The body is completely covered by about forty transverse rows of scales, abdominal rows including about fifteen scales in a row.

The cranial roof is ornamented by a few indefinite longitudinal rugæ.

Material.—The unique holotype, a nearly complete fish, F.18864, in the Australian Museum, Sydney.

Measurements.—The length from tip of snout to base of tail is 66 mm. The trunk has a maximum depth of about 18 mm. The length of the head, including operculum, is approximately 16 mm. Thus the length of the fish is about three and three-quarters the maximum depth, but about four times the length of the head. The depth of the body diminishes rapidly behind the dorsal fin, where the dorsal margin slopes rapidly towards the tail. The fleshy upper lobe of the tail is produced to a length of 9 mm., and at its tip has tapered to the depth of one scale, most of the reduction taking place on the ventral margin.

The principal flank scales are much deeper than long. Those along the lateral line are so greatly broken by crushing against vertebral arches that they cannot be satisfactorily measured, but three scales in the seventh transverse row behind the head and in successive rows below the lateral line have a combined depth of $6\frac{1}{2}$ mm., which is the total length of $5\frac{1}{2}$ of these scales.

Head.—The head is only slightly longer than deep. The orbit, of moderate size, is well above the oral margin and about as far from the back of the operculum as from the snout. The mouth is small but larger than that of some Semionotidæ, and, since the quadrate articulation is below the middle of the orbit, the suspensorium, the operculum, and the lower end of the opercular series are not greatly inclined from the vertical, so that the interoperculum is largely below and not in front of the suboperculum.

The position of the parasphenoid is marked by a prominent thick black ridge of the shape shown in the figure (Text-fig. 1). The impression of the well ossified palate is preserved, without sutures, but displaying its outer margins, which meet in the quadrate at a wide obtuse angle.

Most of the snout is covered by large nasals, which are longer than wide. The long frontals are slightly excavated between the nasals, but widened behind them. Small, nearly square parietals and irregular supratemporals, both bounded behind by wide triangular tabulars, complete the cranial roof.

In the circumorbital series only one bone can be distinguished and that doubtfully—a narrow deep bone just behind the orbit.

The cheek plates are not preserved, having been broken, most probably against the palate. The preopercular canal is preserved, but because of the hinder end of the palate one cannot be certain of the anterior margin of the

preoperculum. The opercular apparatus is long; the operculum, the lower margin of which is nearly straight, is deeper than long and nearly half as deep again as the subopercular. The limits of the interoperculum are not clearly defined and the head is greatly damaged in the region of the branchiostegal rays. There is a well preserved median gular.

The maxilla, placed far forwards from the preoperculum, is not quite clear posteriorly but is obviously deepest there, tapering forwards, with a slightly concave oral margin. The mandible, the upper portion of which is not clearly defined, and none of whose components can be made out, is deepest at the coronoid region and tapers anteriorly. No teeth are preserved. The sensory canals are preserved as casts in the tabulars, preoperculum, and mandible. The supraorbital canal, too, is seen to pass from the nasals to the frontals (where it is concave downwards above the orbit) and to end back in the parietals.

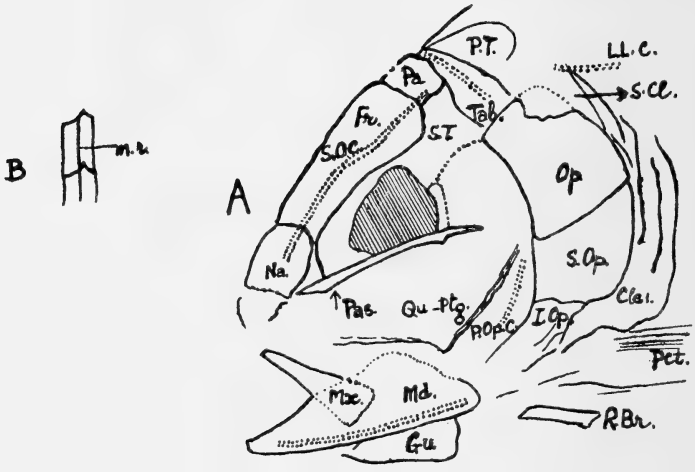


Fig. 1.—*Corunegenys bowralensis.*

A. Sketch of head from No. F.18864. (For lettering see page 147.)

B. Sketch of scales in seventh transverse row behind head and below lateral line.

m.r. = median fold.

Shoulder Girdle.—Triangular post-temporals and deep triangular supracleithra with expanded heads connect to the head the short arcuate cleithra, the triangular anterior ends of which extend forwards beneath the branchiostegal rays and backs of the mandibulæ.

The Trunk and Fins.—The trunk, which is of moderate depth in front of the dorsal fin, is reduced behind that fin by the rapid descent of the dorsal margin. The paired fins are very poorly preserved, and the few rays that remain are more delicate than those of the median fins, where the rays have long, tapering proximal shafts, succeeded by numerous short joints. There is no evidence of distal division of the rays. The long proximal shaft is found in only a few of the middle rays of the caudal fin, the remaining rays being closely articulated to the base. The dorsal fin, comprising thirteen well spaced rays, is almost completely in front of the anal, which is made up of ten similar rays. There are about 23 rays in the caudal fin, the upper fleshy lobe of which is greatly produced.

The Scales.—About forty transverse rows of smooth, thick, ganoine-covered scales invest the body from behind the head to the base of the caudal pedicle,

and abdominally there seem to be sixteen scales in a row—the indefiniteness being due to uncertainty as to the ventral scales and the exact position of the ventral margin. The scales of the well preserved lateral line are crushed down upon the neural and hæmal arches, which show dimly along the body. Some rows below the lateral line are about twice as deep as long, and, displaying their inner surfaces, show a short sharp on their upper margins, no socket, but articulation by means of a median ridge.

Remarks.—Salient points in the structure are, the course of the supra-orbital sensory canal, the shape and size of the maxilla, the steep rise of the dorsal margin of the head, and the squamation.

Explanation of Plate.

A. (?) *Thoracopterus* sp. Pectoral fin, No. U.S.G.D. 151, Geological Museum, University of Sydney. $\times 1\frac{1}{2}$.

B. *Corunegenys bowralensis* sp. nov. The unique type, No. F.18864, Australian Museum, Sydney. $\times 1$.

Text-fig. 1.—*Corunegenys bowralensis* sp. nov. No. F.18864, Australian Museum, Sydney.

A. Head. $\times 3$.

Clei. = Cleithrum.
Fr. = Frontal.
Gu. = Gular.
I.Op. = Interoperculum.
L.L.C. = Lateral line canal.
Md. = Mandible.
m.r. = Median fold.
Mx. = Maxilla.
Na. = Nasal.
Op. = Operculum.
Pa. = Parietal.
Pas. = Parasphenoid.
Pct. = Pectoral fin.
P.Op.C. = Preopercular canal.
P.T. = Post-temporal.
Qu.-Ptg. = Quadrato-pterygoid.
R.Br. = Branchiostegal rays.
S.Cl. = Supra-cleithrum.
S.O.C. = Supraorbital canal.
S.T. = Supratemporal.
Tab. = Tabular.

B. Scales in seventh transverse row behind head and below the lateral line. $\times 3$.

STUDIES ON THE CULTIVATION OF THE TUNG OIL TREE, *ALEURITES FORDII.*

Part II. Study of a Heavy Yield of Fruit obtained on the North Coast of New South Wales.*

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(*Manuscript received, October 18, 1941. Read, November 5, 1941.*)

Contents.

	Page
Introduction	148
Plantation at Coramba	149
Establishment of the Trees	149
General Yield	150
Yield Studies	150
Number of Fruits per Tree	152
Fruit Analyses	152
Variation in Husk, Seed-coat and Kernel	153
Variation in Oil Content	154
Oil Analyses	154
Acknowledgments	155
References	156

Introduction.

The cultivation of the Tung Oil tree, *Aleurites fordii*, has been investigated by officers of the Sydney Technological Museum since 1923. The early results were obtained from a study of individual trees,[2] but by 1937 it became possible to study a commercial grove, one owned by Mr. A. H. Woolcott at Bargo, 62 miles south of Sydney.[4]

In pursuance of this study another commercial grove was selected, that of Mr. C. J. Frank at Coramba, 390 miles north of Sydney. This grove proved ideal in many ways. In the first place it is, as far as we can ascertain, the best yielding grove in Australia and, secondly, the trees are remarkably uniform in character. The returns have proved very profitable to this enthusiastic and painstaking grower.

In view of the serious position confronting the tung oil industry generally through inability to obtain commercial supplies from China, the results obtained in the study of Mr. Frank's grove are of considerable national importance. The commercial return from his two paddocks (A and B), of about two acres extent, for the present year is a record for Australia, and probably for the world.

* Part I appeared This Journal, 1940, *74*, 42.

Plantation at Coramba.

This consists of approximately two acres of bearing trees, and in addition, about six acres of young trees. At the time the plantation was first visited, in October, 1940, the trees were in flower, and the uniformity of the flowering, the scarcity of the male-flowering type of tree, and the remarkable robustness and vigour of the trees were impressive. A good yield seemed to be indicated, and it was decided to keep the grove under close observation.

A second visit was made in February, 1941, when the fruit crop was half grown. The trees were so heavily laden that a high yield seemed certain, and in June-July of this year a special effort was made to record accurately the yield figures, and at the same time samples were taken for study in the laboratory.

The plantation comprises two small paddocks of mature trees, details of which are given in Table I. Paddock A is situated on the west side of the railway, on a north-east slope. It is protected by a railway embankment on the east, and may gain some advantage in drainage from calf and pig pens adjacent. The soil is a clayey loam, possibly of basaltic origin. The surface soil, about 9 inches deep, is rich in humus; the subsoil is very deep. The actual area of this paddock is 80 ft. $\times$ 336 ft., or approximately five-eighths of an acre.

Paddock B is situated on the east side of the railway. Its aspect and soil are similar to those of Paddock A, but it receives no special advantages. The area is approximately $1\frac{1}{4}$ acres.

Table I.

Details of Tung Plantation.

	Paddock A.	Paddock B.
Area	$\frac{5}{8}$ acre.	$1\frac{1}{4}$ acres.
Aspect	North-east.	North-east.
Soil	Clay loam.	Clay loam.
Source of seed	"Whittell."	"Whittell" and Queensland Forests.
Seed sown	October, 1934.	October, 1933, and October, 1934.
Density of trees ..	170 per acre.	180 per acre.

The Establishment of the Trees.

Paddock B contains two plantings of trees. In 1933 seed was obtained from Queensland Forests Limited, and the seedlings planted out the following October, the planting being on the square system, 22 ft. apart, equivalent to 90 trees per acre.

The following year, 1934, further seed was supplied by the "Farmer and Settler" Newspaper. This seed was apparently derived from stock known as Pennant Hills Trees.[4] The seedlings were planted in September, 1935.

In Paddock B the original planting seemed so open that additional rows were interplanted, a new seedling being placed in the centre of each square, making a total planting of 180 trees per acre. In all, Paddock B contains 222 trees, but over twenty of these, affected by poor drainage, yielded very little fruit.

Paddock A consists entirely of trees from the Pennant Hills seed, sown in 1934 and planted out in October, 1935. The planting method adopted was to "stagger" the rows, to give a triangular system, planting distances of 16 ft.

between rows and 16 ft. between trees in the row, being equivalent to 170 trees per acre.

The land, which was first cropped in 1933 to pumpkins, after being given a dressing of lime, was planted with potatoes in 1934, and the seedlings of Tung were planted in the growing potato crop. The following year a crop of soya beans was raised between the rows, and intercropping has been practised until the growth of the trees has made this impossible. Sheep have been used for feeding off the haulms of soya beans and other intercrops and to keep down weeds. Young pigs have also had access to the paddock.

Paddock B was first cropped with barley, then potatoes, and finally soya bean. The Tung seedlings were planted in the barley. In the present condition of the trees, intercropping or any cultivation between the rows is quite impossible. The weeds and undergrowth are kept down by sheep. Pruning or any interference with the normal growth of the trees has been avoided.

The climate at Coramba is well suited to tung, both in regard to the high rainfall experienced, and the rare occurrence of frosts after September. The average annual rainfall at Coramba over a three-year period (1938-1940 inclusive) was 49·89 inches, and the distribution is such that the greater part of this rainfall occurs during the growing season, October to April. During the seven-month period October, 1940-April, 1941, when the heavy crop was being carried, Coramba received 36·95 inches of rain.

The close planting adopted by Frank appears to have several advantages over the wider spacings. Some of these advantages may be enumerated :

(1) The heavy growth of leaf and other debris which covers the ground during the winter adds appreciably to the humus intake of the soil, and effectively prevents moisture loss. Tung appears to respond to a high humus and nitrogen content in the soil.

(2) The trees provide their own protection from wind and weather damage.

(3) Growth of the trees does not appear to be adversely affected in any way.

General Yield.

The first fruit was obtained from the trees in 1937 ; they were then three years old, but this yield was very small. In 1938 an appreciable yield was obtained. The year 1939 was apparently a favourable season, for a good yield, double that of the previous year, was obtained. The yield was not so good in 1940. A late frost is said to have caused a big reduction in fruit setting, whilst the reduced yield may also have been a reaction to the high yield of the previous year. An exceptionally high yield of 12,291 lb. net of dry fruit was obtained during the present year (1941). On decortication, 6,145 lb. of seed was separated. The seed yielded on expression approximately 2,300 lb. of oil, or 18·0% of the whole fruit.

Yield Studies.

When we visited Coramba at the end of June, 1941, for the purpose of recording the actual yield, the fruit had mostly fallen from the trees, although here and there occasional trees were still holding perhaps fifty per cent. of their crop. The hanging fruit, however, appeared mature, and was easily shaken down. Underneath, the ground was thickly covered with fallen leaf débris, amongst which the fruit was lying. Under such conditions the fruit would remain wet for a long time, and proper drying would require the collection and spreading of the fruit on open ground.

Yields from Paddock A.

Paddock A, which on casual inspection promised the higher yield, was selected for the most detailed study, but it is a matter for regret that time did not permit of equal attention being given to Paddock B. In the time at our disposal, it was quite impossible to collect all the fruit from Paddock A. Four plots, each equivalent to ten trees or one-seventeenth of an acre, were marked out for the purpose of estimating the yields. These plots were marked out across the paddock, along the butt lines of two rows, with one included row, and comprised the fruit lying on the ground under five whole trees and ten half trees. Plot IV included the equivalent of eleven whole trees, but the yield from this plot has been reduced by the fraction 10/11 for the purpose of this analysis.

The overlapping of adjacent trees made the collection of the fruit from individual trees quite impossible. The fruit from each plot was collected separately, weighed in the field, and spread in open grassland to dry. Corrected yield figures were obtained from a re-weighing when the fruit appeared thoroughly dry and ready for bagging. The results of these yield figures are given in Table II, together with figures for oil yield, which have been calculated from analyses of five samples from each plot. The mean yield per plot of 524 lb. of dry fruit and 113 lb. of oil is equivalent to yields of 3·98 tons and 1,960 lb. of fruit and oil respectively per acre.

The moisture content of the fruit at time of collection and the consequent loss of weight on drying varied considerably between plots, depending on their positions. Plot 1, near the southern end of the paddock, was the most exposed, and had a lighter covering of leaf litter. The fruit was, in consequence, relatively dry when collected.

TABLE II.

Yield of Fruit from Plots.

Plot.	Yield of Fruit.		Oil Yields on Air Dry Fruit.[1] Per cent.	Oil Yields Cal. from Columns 3 and 4. Lb.	Mean Weights of 600 Fruits as Collected. Lb.	Number of Fruits per tree Cal. from Columns 2 and 6.
	As Collected.	Air Dry.				
A1	692	531	20·86 ±0·71	110·9	37·25 ±1·11	1,113
A2	828	547	22·32 ±0·21	122·0	43·75 ±2·21	1,135
A3	768	514	22·04 ±0·62	113·3	48·75 ±1·70	945
A4	804	503	21·45 ±0·34	108·0	49·60 ±2·94	972
Means	773 ±29·7	542 ±9·7[2]	21·67 ±0·28	113·5[2]	44·84 ±1·10	1,041
B1	467	373[3]	19·34 ±1·66	72·1[3]	42·0 ±2·74	606·5

[1] Means of analyses from five trees in each plot.

[2] Equivalent to a yield of 3·98 tons of fruit, and 1,960 lb. of oil per acre.

[3] Equivalent to a yield of 2·66 tons of fruit, and 1,250 lb. of oil per acre.

Number of Fruits per Tree.—The impracticability of studying the yields from individual trees has already been pointed out. Since many yields given in the literature are calculated on the number of fruits per tree,[2] an estimation of this figure was thought to be desirable. Whilst the fruit was being collected, counted lots of 600 fruits were weighed in the field, four replications of such counts being made for each plot. The number of fruits per tree in each plot was calculated from the mean weight of the fruit and the total weight of the half-dry fruit. Details are included in Table II. The average yield per tree exceeds 1,000 fruits. A yield approaching this figure has often been desired but has rarely been obtained, and this only on individual isolated trees (e.g. Grafton).

Yields from Paddock B.

In Paddock B a single plot of more or less equivalent size to those in Paddock A was marked out for the purpose of comparison. Owing to the different arrangement of the trees, the plot is not exactly equivalent, as it includes the fruit lying under five whole trees and twelve half trees, and equal to one-sixteenth of an acre. The ground was covered with less fruit débris and the fruit was more exposed and in a drier condition. The yield of 373 lb. of air-dried fruit from the plot is equivalent to 2·66 tons per acre. Details of the yield and number of fruits per tree are included in Table II.

The yield from this plot is considerably lower than from those in Paddock A, but must still be regarded as very good. The yield from the whole of Paddock B would be lower than that indicated by the plot yield, because of the inclusion of the poor trees at the southern end, already mentioned.

Fruit Analyses.

Analyses of the proportion of husk, seed-coat, kernel, and oil in samples of fruit from a few individual trees at Bargo, reported previously[4] indicated that considerable variation in these characteristics occurs. Similar results have been reported by authors in other parts of the world.[4][1] Trees situated at Bargo were particularly favourable for this work by reason of their diverse origin. Further work on the trees at Bargo which had been anticipated had to be abandoned because of the severe drought conditions experienced in that district, and the almost complete failure of the Tung crop, and in fact, of all other crops. Until conditions in the district improve, the work at Bargo cannot be continued.

The trees at Coramba offer a more limited scope in this study, the plantation being less extensive, the trees of less diverse origin and far more uniform in all characters.

Five samples of twenty fruits each were taken from each plot in Paddock A and from the one plot in Paddock B, for the purpose of these analyses and for work on the yield and quality of the oil. The fruits were taken from directly under the individual trees concerned, where possible mixture with fruit from adjacent trees was least likely. No attempt at selection of fruit was made. In addition, fruit from one tree selected on the basis of attractive fruit type was included. In this case, only well-developed, large fruits were collected. These fruits characteristically split readily on drying.

At the time of collection, the fruit was still partially wet, and it was allowed to air-dry in the open for several weeks before analyses were commenced. The analyses were carried out over a period of two months, and considerable differences in the moisture content of the husk and seed were found. For the sake of uniformity, the results given have been calculated on moisture-free basis. The fruits generally are of good *Aleurites fordii* type, smooth or slightly furrowed between the sections, rarely rough and deeply furrowed. Fruits consist normally

of five sections, occasionally of four, and rarely of six. In each section there is one kernel; very exceptionally twin kernels occur. The kernels were mostly sound and plump, but in some samples were soft and shrivelled, and occasional seeds were empty of kernel.

Variation in Husk, Seed-Coat and Kernel.

The general uniformity in the proportion of husk, seed-coat and kernel between the plots in Paddock A is remarkable, and in conformity with that of the trees and their fruit. In Table III detailed figures are given, and these show that on a moisture-free basis, the proportion of kernel varies from 39·6% to 41·7% between plots, and that these differences are scarcely, if at all, significant.

In Paddock B, on the contrary, the proportion of kernel is appreciably low, and the husk is correspondingly thick. In the analysis of fruits, it has become obvious that the seed-coat does not vary to any marked extent, and that variation is accounted for by changes in the proportion of outer husk to kernel.

Comparison of these analyses with those previously reported from Bargo shows a much higher proportion of kernel in the Coramba fruit. Two samples of Bargo fruit analysed concurrently also show a high percentage of husk, which seems typical of the Bargo fruit. Analyses of a sample of fruit from the two historic trees at Grafton Experiment Farm,[(2)] which are now approximately twenty years old, give figures comparable with the Coramba results, and decidedly superior to the Bargo results.

TABLE III.

Means of Analyses of Fruit Samples.

Plot.[1]	Mean Weight Whole Fruit.[1]	Composition of Fruit.[1]			Oil in[1] Kernel Per cent.	Oil Yield[1] in Whole Fruit Per cent.
		Husk Per cent.	Seed Coat Per cent.	Kernel Per cent.		
A1	21·78 ±0·27	31·90 ±1·03	27·44 ±0·55	40·66 ±0·71	58·56 ±0·38	23·85
A2	23·61 ±0·95	32·04 ±0·44	26·74 ±0·62	41·22 ±0·47	60·26 ±0·50	24·83
A3	24·64 ±0·61	32·68 ±1·29	25·58 ±0·42	41·74 ±1·05	59·80 ±1·42	24·95
A4	22·81 ±0·72	33·75 ±0·67	26·63 ±0·42	39·62 ±0·66	59·78 ±0·46	23·68
B1	24·66 ±1·92	42·02 ±1·57	23·12 ±1·55	34·86 ±1·10	62·60 ±3·58	21·81
8-1[2]	30·97	36·8	22·0	41·2	62·1	25·60
Grafton[3]	22·92	31·7	27·3	41·0	58·2	23·85
W1/4-11[4]	33·90	42·8	24·7	32·5	58·5	19·00
W1/6-11[4]	33·10	44·4	23·4	32·2	60·2	19·40

[1] Calculated on moisture-free basis.

[2] A tree selected on basis of its large, attractive fruit.

[3] Mixed fruit from two old Grafton trees.

[4] Five-year-old trees at Bargo, derived from the Grafton parents.

The moisture content in the husk, seed-coat, and kernel shows a certain degree of variation. In the husk this averaged from 13·0% to 21·7%, and in the seed-coat from 10·7% to 16·5%. The moisture content of the kernels showed a normal range from 2·6% to 8·2%, although two exceptional samples had moisture contents of 16·5% and 30·2%. The reason for this high moisture content is not apparent, and does not seem entirely due to the state of dryness of the whole fruit. It may be due to premature falling of the fruit or some other cause.

Slight but barely significant differences in proportion of kernels to husk are found between the samples from individual trees, the range being from 38·8% to 45·3% of kernel in Paddock A, and 31·4% to 38·2% in Paddock B. These results differ from results reported by many workers, who have found very considerable differences between individual trees. In view of the comparative uniformity in the husk-kernel ratio, and of the uniformity of the trees in other characters, e.g. vigour, habit of growth, absence of the undesirable "male" trees, uniform cluster-fruiting type, it must be presumed that the trees are of a relatively pure strain, compared with other plantations seen in New South Wales.

The sample from tree marked 8-1 is worthy of mention. In spite of the definite selection of large, well-formed and well-developed fruit, it gives, weight for weight, no higher proportion of kernel than the other samples, which frequently included small and deformed fruits.

The frequently reported correlation between high kernel proportions and large fruit size does not appear to be borne out by the figures obtained here. The mean weight of the fruit was from 20·2 to 31·1 gms., but the kernel content appears to have no relation to this mean weight.

Variation in Oil Content.

In Paddock A, the uniformity of the oil content of the kernels is notable, and contrary to the usual findings. Even the sample A 5-3, which had 16% moisture in the kernel, was little inferior to its adjacent trees. In Paddock B, a greater variation in oil content is shown, which might be expected, as trees include two origins. The oil content in the dried kernel varies from 57·1% to 61·6% in Paddock A, and from 51·7% to 69·1% in Paddock B.

Oil Analyses.

The kernels separated from the various samples of fruit enumerated in Table III were examined for yield and quality of oil. The quantities available were not sufficient for mechanical extraction of the oil, and, consequently, the comminuted kernels were treated with ethyl ether in a Soxhlet extractor. Whatever slight differences might result from the two methods of treatment, the results of analyses are strictly comparable. Solvent extracted oils have, in our experience, given reasonably satisfactory results, although the Browne Heat Tests are invariably high. For purposes of comparison the results are set out in tabular form. (See Table IV.)

No explanation can be offered at present for the variation in chemical composition of the individual oils, as revealed by the refractive indices and heat tests. At the same time, the specific gravities of the oils are quite normal. The chemical composition of these oils will be the subject of a separate investigation. Meanwhile the following facts should be specially noted:

(1) Although only one plot from Paddock B was examined, as against four plots from Paddock A, there is sufficient evidence to indicate that the oil from the drier Paddock B is of superior quality to that obtained from Paddock A, which is much wetter, and in which the soil appears richer in humus and nitrogen.

TABLE IV.

Physical Characters of Oils.

Sample.	$d\frac{15\cdot5^\circ}{15\cdot5^\circ}$	$n_D^{25^\circ}$	Acid Value.	Browne's Heat Test.	Remarks.
A 5-1	0·940	1·5100	0·53	19½ mins.	
5-2	0·939	1·5123		15½ mins.	
5-3	0·940	1·5110	15·2	Did not gel.	Spongy kernels.
5-4	0·939	1·5136		14¾ mins.	
5-5	0·940	1·5013	0·73	17½ mins.	
A 8-1	0·941	1·5169		13 mins.	Crumbly "gel".
9-1	0·940	1·5148		14¾ mins.	
9-2	0·939	1·5117		16½ mins.	
9-3	0·939	1·5120	0·54	16 mins.	
9-4	0·939	1·5127		15 mins.	
9-5	0·939	1·5117		16 mins.	
A 13-1	0·939	1·5126	1·2	14½ mins.	Kernels spongy.
13-2	0·942	1·5153		11¾ mins.	Firm "gel".
13-3	0·939	1·5125		15¼ mins.	
13-4	0·941	1·5150		14 mins.	
13-5	0·940	1·5147	0·45	14¼ mins.	
A 19-1	0·940	1·5142		14 mins.	Firm "gel".
19-2	0·939	1·5120	1·04	16 mins.	
19-3	0·939	1·5117		18½ mins.	
19-4	0·940	1·5143	0·45	13¼ mins.	
19-5	0·939	1·5127		15 mins.	
19-6	0·940	1·5110	0·57	17½ mins.	
B 8-3	0·939	1·5118	0·68	16½ mins.	
8-4	0·942	1·5172		10¾ mins.	Crumbly "gel".
8-5	0·941	1·5157		14¼ mins.	Firm "gel".
7-6	0·942	1·5167		12 mins.	Crumbly "gel".
9-6	0·942	1·5170		11 mins.	Crumbly "gel".

(2) The oil obtained from the mixed fruits from both paddocks by expression is of excellent quality, and meets the requirements of the Australian Standard Specification.

(3) An average sample from the two paddocks taken from a total volume of 240 gallons, the product from 12,291 lb. of dried fruit collected from the two acres, gave the following results on examination :

$d\frac{15\cdot5^\circ}{15\cdot5^\circ}$	0·940
$n_D^{25^\circ}$	1·5164
Acid value	0·72
Saponification number	193·4
Iodine number (Wijs 2 hours)	164·4
Browne's heat test	12 minutes.

ACKNOWLEDGMENTS.

Our thanks are due to Mr. C. J. Frank for placing his grove at our disposal.

References.

(1) Mowry, H. : Univ. Florida Agric. Exp. Station, Bulletin No. 247, 1932.

(2) Penfold, A. R., and Morrison, F. R. : Syd. Tech. Mus. Bulletin No. 12, 1940.

(3) Potter, G. F., Angelo, E., Painter, J. H., and Brown, R. T. : Proc. American Soc. of Horticultural Science, 1940, *37*, 515.

(4) Smith-White, S. : Jour. Proc. Roy. Soc. N.S.W., 1940, *74*, 42.

THE STEREOCHEMISTRY OF SOME METALLIC COMPLEXES, WITH SPECIAL REFERENCE TO THEIR MAGNETIC PROPERTIES AND THE COTTON EFFECT.

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In recent investigations dealing with the stereochemistry of metal complexes Pfeiffer, Christelheit, Hesse, Pfitzner and Thielert (1938) and French and Corbett (1940) have used observations on rotatory dispersion as a basis for drawing conclusions concerning the orientation of valence bonds about metal atoms. As these are the first attempts, so far as the author is aware, to use rotatory dispersion measurements for this purpose, it is of some interest to check the findings based on rotatory dispersion studies against those based on other physical methods. Attention has already been drawn to the fact that some of the conclusions reached by Pfeiffer and his collaborators are not those one would have anticipated from the results of magnetic measurements made in this laboratory, on closely related compounds. (Mellor, 1941.)

In certain favourable instances, bond type and orientation can be determined from magnetic data. This can be done with greatest certainty in the case of the diamagnetic complexes of nickel, because for these, the results of magnetic studies have been verified by X-ray crystal analysis (Cox, Wardlaw and Webster, 1935 ; Elliott, 1938 ; Brasseur, 1938 ; Peyronel, 1941), synthesis of isomers (Tschugaeff, 1910 ; Sugden, 1932*a*) and studies of crystal optics (Mellor and Quodling, 1936). For this reason most attention has, in the present investigation, been paid to compounds of nickel ; reference is however made to compounds of several other metals. The conclusions from magnetic measurements will be discussed first, and then, in some detail, the bearing of these conclusions on the optical data (dispersion and absorption).

The Compounds Investigated.

The compounds on which susceptibility measurements have been made are listed in the first column of Table I. With one exception, their preparation has been previously described by Pfeiffer *et al.* (1941), Lifschitz (1922) and others. The structures proposed by these authors for the different compounds (numbered as in Table I, except for XI) are shown as follows : compounds I, II and III, Fig. I ; IV and XI, Fig. 2A and 2B respectively ; V, VI and VII, Fig. 3 ; IX and X, Fig. 4.

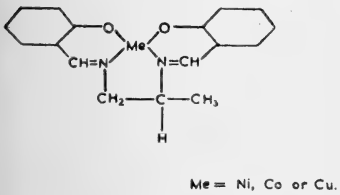

Fig. 1.

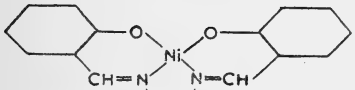

Fig. 2A.

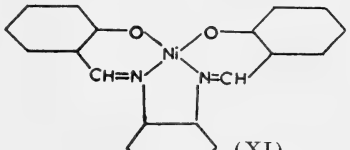

Fig. 2B.

TABLE I.

Results of Susceptibility Measurements.

Compound.	Specific Susceptibility $\varkappa \times 10^6$	Molar Susceptibility $\chi_M \times 10^6$	Diamagnetic Correction Applied. $\times 10^6$	Temperature. °K.	Magnetic Moment, μ Bohr Magnetons.	Number of Unpaired Electron Spins.
I. $C_{17}H_{16}O_2N_2Ni$ Bis - salicylaldehyde - propylene - diimine - nickel	−0·1	Diamagnetic	—	—	~0	0
II. $C_{17}H_{16}O_2N_2Co$ Bis - salicylaldehyde - propylenediimine - cobalt	7·20	2,440	−174	293	2·48	1
III. $C_{17}H_{16}O_2N_2Cu$ Bis - salicylaldehyde - propylenediimine - copper	3·26	1,120	−174	295	1·76	1
IV. $C_{20}H_{14}O_2N_2Ni$ Bis - salicylaldehyde - o - phenylenediimine - nickel	−0·2	Diamagnetic	—	—	~0	0
V. $C_{22}H_{30}O_4Ni$ Bis - formylcamphor - nickel	9·72	4,050	−245	287	3·15	2
VI. $C_{22}H_{30}O_4Co2H_2O$ Bis - formylcamphor - cobalt dihydrate ..	23·8	10,785	−266	286	5·05	3
VII. $C_{22}H_{30}O_4Cu.C_4H_8O_2$ Bis - formylcamphor copper + dioxane of crystallisation ..	2·42	1,233	−304	288	1·89	1
VIII. $C_{33}H_{45}O_6Co$ Tris-formyl camphor cobalt	0·33	199	−369	290	1·15	0
IX. $C_{24}H_{34}O_2N_2Ni3H_2O$ Bis-formyl camphor-ethylenediimine-nickel trihydrate ..	−0·4	Diamagnetic	—	—	~0	0
X. $C_{24}H_{34}O_2N_2Cu2H_2O$ Bis - formylcamphor-ethylenediimine copper dihydrate ..	3·27	1,574	−294	288	2·08	1

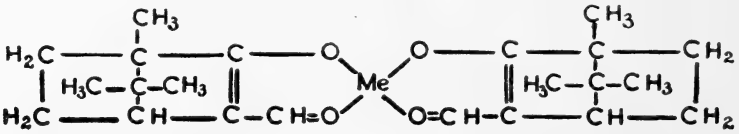

Fig. 3.

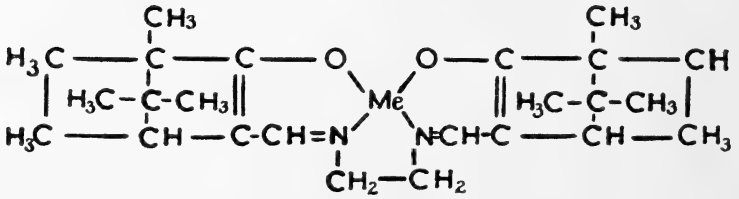

Fig. 4.

The structures shown are in accord with the general theory concerning the formation of chelate compounds, confirmation of which has been obtained by various physical methods, including crystal structure analyses.[1]

The main point at issue in the present work, however, relates to the character and orientation of the bonds by which the various organic groups are attached to the metal atoms.

In order to arrive at a decision as to which of the various alternatives (as regards orientation and bond character) obtains in a given complex, the measured magnetic moment of the metal atom (see Table I) is compared with that predicted by Pauling and Huggins (1931) for the different bond types. A portion of the table of predicted moments, relevant to the present work, is reproduced in Table II below.

TABLE II.

Electron Spins Predicted for Different Bond Types (Pauling and Huggins).

Metal Atom.	For ionic or sp^3 tetrahedral bonds.	For square dsp^2 bonds.	For octahedral dsp^3 bonds.
Ni^{II}	2·83	0·00	—
Cu^{II}	1·73	1·73	—
Co^{II}	3·88	1·73	—
Co^{III}	4·9	2·83	0·00

The sixth column of Table I shows the magnetic moments of the metal atoms as deduced from the data tabulated in the preceding columns of the table. These moments will form the basis of the discussion to follow.

EXPERIMENTAL AND NOTES ON TABLE I.

Preparation of Compounds.—The methods of preparation employed were substantially those used by earlier workers. In preparing (I), (II) and (III) optically inactive propylenediamine was used. The formyl camphor used in the preparation of (V), (VI), (VII), (VIII), (IX) and (X) was prepared from synthetic camphor and was therefore optically inactive. In order to check its identification and purity, each compound was analysed for metal content. The results of the analyses which were kindly carried out for me by Dr. G. Burger of the University of Adelaide are set out in Table III.

Magnetic Measurements.—Magnetic susceptibility measurements were made by the Gouy method, a detailed account of which has been given by Sugden (1932*b*).

In calculating magnetic moments the substances were treated as "magnetically dilute"; Curie's Law was assumed to hold good in each case. Owing to the smallness of $\triangle W$ for the diamagnetic compounds (I), (IV) and (IX), and the consequent uncertainty in κ, calculations of molar susceptibilities and moments for these compounds have been omitted.

Absorption Measurements.—These were made by means of a Hilger-Nutting spectrophotometer. Full details of the method used have been given by Twyman and Allsopp (1934).

[1] Relatively few crystal analyses have been made on internal complexes, the type of compound with which this communication is mainly concerned. It is therefore of interest to note that confirmation (Peyronel, 1941) of the theory of internal complex formation has been obtained with the recent complete determination of the crystal structure of N–N^1 dipropyldithiocarbamate nickel. In this diamagnetic substance nickel is square coordinated.

TABLE III.

Substance.	% Metal Found.	% Metal Calculated.
I. $C_{17}H_{16}O_2N_2Ni$	17·4	17·3
II. $C_{17}H_{16}O_2N_2Co$	17·2	17·4
III. $C_{17}H_{16}O_2N_2Cu$	18·5	18·6
IV. $C_{20}H_{14}O_2N_2Ni$	15·7	15·75
V. $C_{22}H_{30}O_4Ni$	14·4	14·1
VI. $C_{22}H_{30}O_4Co2H_2O$	12·9	13·0
VII. $C_{22}H_{30}O_4CuC_4H_8O_2$	12·5	12·5
VIII. $C_{33}H_{45}O_6Co$	9·75	9·88
IX. $C_{24}H_{34}O_2N_2Ni3H_2O$	11·9	11·9
X. $C_{24}H_{34}O_2N_2Cu2H_2O$	13·2	13·2

THE STRUCTURE OF METAL COMPLEXES AS DETERMINED FROM MAGNETIC DATA.

Nickel.

The compounds of nickel fall into two classes, the first of which includes compounds (I), (IV) and (IX), which are diamagnetic. In these three compounds, the four bonds linking the nickel atom to the chelate molecule are both covalent and coplanar. This conclusion is consistent with the fact that all attempts to resolve compound (XI) (see Fig. 2B) which, except for the substitution of a carboxyl group, is identical with (IV) (Fig. 2A) have failed (Pfeiffer *et al.*, 1938). If nickel is square coordinated in (XI) resolution into optical isomers is impossible.

The magnetic data also make it clear why Pfeiffer and his collaborators failed to resolve bis-salicylaldehyde-propylenediimine-nickel (I) when prepared from bis-salicylaldehyde nickel and *optically inactive* propylenediamine. If the bonds about the nickel atom in bis-salicylaldehyde-propylenediimine-nickel were tetrahedrally oriented, the following isomeric forms would be theoretically possible :

dD lD
lL dL

D and L refer to the configuration or the nickel atom, d and l to the configuration of the asymmetric carbon atom (asterisked in Fig. I). Repeated fractional crystallisation failed to bring to light any isomeric forms and Pfeiffer (1938) thus concluded that the nickel bonds were coplanar.

The only paramagnetic nickel compound studied in the present work was bis-formylcamphor-nickel (V), the susceptibility of which indicates that the nickel atom contains two unpaired electrons. Although the prediction (Pauling, 1931) regarding the structure of paramagnetic nickel complexes has not yet been very satisfactorily verified by either chemical or physical methods,[2] it is concluded that, in bis-formylcamphor-nickel, the metal atom is tetrahedrally coordinated.

[2] The high electric dipole moment of paramagnetic $[Ni(NO_3)_2(Et_3P)_2]$ (Jensen, 1936) can be accounted for by assuming that the complex possesses a tetrahedral configuration.

Cobalt.

Bis-salicylaldehyde-propylenediimine-cobalt (II) has a moment of 2·4 Bohr magnetons which, when due allowance is made for orbital contribution, indicates that the cobalt atom contains one unpaired electron; this is the number of unpaired electrons predicted (Pauling, 1931) for square coordinated Co^{II}. The planar structure of tetracovalent cobaltous complexes with one unpaired electron has not yet been verified by other physical methods or even by the synthesis of isomers, but the success, to date, of the stereochemical predictions based on magnetic data, for other metals, makes the planar structure of bis-salicylaldehyde-propylenediimine-cobalt fairly certain.

Bis-formylcamphor-cobalt^{II} dihydrate (VII) is, by the magnetic criterion, an ionic complex, that is to say, the bonds linking cobalt to the surrounding oxygen atoms (octahedrally arranged) are predominantly ionic in character. The effect of this type of linking on certain optical properties of the compound will be discussed in a later section of the paper.

Tris-formylcamphor-cobalt^{III} is weakly paramagnetic,[3] and in this respect it resembles tris-acetylacetone-cobalt^{III} (Takagi and Ishiwara, 1914). The paramagnetism of both these compounds is too small to be accounted for by unpaired electron spins in the cobaltic atom and is to be attributed to unquenched orbital moment. The cobalt atom in tris-formylcamphor-cobalt^{III} forms d^2sp^3 bonds with the six surrounding oxygen atoms, as in potassium cobalt-ioxalate (Johnson, 1932).

Copper.

While magnetic data enable one to distinguish between cupric and cuprous copper, the latter of which is tetrahedrally coordinated, they do not permit one to draw any conclusions about the configuration of the cupric atom. There is, however, much evidence, chiefly from the X-ray analysis of crystals, to show that cupric copper forms square complexes. Square complexes have been found in the crystals of $K_2CuCl_4 2H_2O$ (Chrobak, 1934), $CuCl_2 2H_2O$ (Harker, 1936), CuO (Tunnel, Posnjak and Ksanda, 1935), $CuSO_4 5H_2O$ (Beevers and Lipson, 1934), $CuPy_2Cl_2$ (Cox, Sharatt, Wardlaw and Webster, 1936), and $Cu(C_4H_7O_2)$ (Cox and Webster, 1935). In the absence of factors known to change this form of bond orientation, Cu^{II} will show uniform stereochemical behaviour, an assumption that can equally well be applied to other atoms such as Pt, Pd, Au, etc., for which square coordination has been firmly established. If a metal atom is to form square bonds, a *d* orbital must be available for bond formation. Although this is a necessary condition, it is not a sufficient one. The two disturbing factors at present known are steric effects of the kind observed in complexes formed with certain substituted pyrromethenes (Porter, 1938; Mellor and Lockwood, 1940), and also effects arising from pronounced electronegativity differences[4] between the bonded atoms. Probably the more generally concerned factor is the electronegativity difference between the metal atom and the four surrounding non-metal atoms. Certain metal atoms, Ni^{II} Co^{II} and Mn^{II}, for example, are more sensitive to electronegativity differences than others, in so far as the effect of such differences on the bond type is concerned. With the possible exception of its compound with phthalocyanin (Klemm and Senfr, 1939), no instance of a square Mn^{II} complex has yet been reported; instances of square bonding are fairly common among the compounds of Ni and Co and quite common among those of Cu^{II}. As already pointed out, Cu^{II} forms square bonds in CuO, $CuSO_4 5H_2O$ and $CuCl_2 2H_2O$; in the analogous compounds of Co^{II} and Ni^{II} no such bonds are found. It is only in the case of extreme

[3] I am indebted to Mr. D. P. Craig for the preparation and measurement of this substance.

[4] The term electronegativity is here used in the sense defined by Pauling (1940).

electronegativity differences between the bonded atoms, as between Cu^{II} and F, the most electronegative of all atoms, that square coordination of Cu^{II} fails to appear. Thus CuF_2 is an essentially ionic crystal with the fluorite structure. (Ebert, 1931.) Palladium is similar to copper in regard to its tendency to form square bonds, the only exception being PdF_2, which has the rutile structure. (Ebert, 1931.) Since neither steric nor electronegativity factors are likely to affect the bond type in bis-salicylaldehyde-propylenediimine-copper (III) and bis-formylcamphor-ethylenediimine-copper (X) it is concluded that in each of these compounds the copper is square bonded.

The Structure of Metallic Complexes in Relation to the Cotton Effect.

It is in regard to the structure of the compounds containing optically active chelate groups that the conclusions based on magnetic data fail to accord with those based on rotatory dispersion measurements. The situation is briefly this. Pfeiffer and his collaborators (1938) infer that, because bis-salicylaldehyde-d-propylene-diimine-nickel shows the Cotton effect, the Ni atom is tetrahedrally coordinated. This latter inference is based on the assumption that for the Cotton effect to appear, a molecule like that of (I) must contain, in addition to the asymmetric carbon atom, a chromophoric metal atom—also with an asymmetric (tetrahedral) configuration. The inactive form of (I) which contains equal numbers of *d* and *l* asymmetric carbon atoms is *diamagnetic*. (See Table I.) This simply means that in the molecule of (I) the four bonds to the nickel atom are coplanar, irrespective of whether the molecule contains a *d* or *l* propylene-diamine residue.

French and Corbett, making use of the same assumption, viz. that the existence of a tetrahedrally coordinated chromophoric metal is necessary for the production of the Cotton effect—have come to the conclusion that nickel is tetrahedrally coordinated in *paramagnetic* bis-d-formylcamphor nickel. In other words rotatory dispersion measurements have been used to show that both para and diamagnetic nickel complexes contain tetrahedrally coordinated nickel.

Two important questions seem to be involved here :

(1) There is first of all the question as to whether the metal complexes with anomalous rotatory dispersion really show the Cotton effect.

(2) Assuming that the Cotton effect appears in diamagnetic nickel compounds, the question then arises as to whether there is not some way of accounting for its appearance which does not involve the assumption of a tetrahedrally coordinated nickel atom. In attempting to answer these questions it is necessary to consider briefly the nature of the Cotton effect itself.

The Cotton Effect.

Three phenomena are associated with the Cotton effect. A substance exhibiting it shows (*a*) anomalous rotatory dispersion ; (*b*) zero rotation in the neighbourhood of the maximum of an absorption band ; (*c*) circular dichroism with the maximum ellipticity in the region of zero rotation (or maximum absorption). Measurements of circular dichroism afford the most certain means of detecting the Cotton effect (Bruhat 1930), but, in their absence, measurements of both absorption and rotatory dispersion may be used.

With regard to the first question mentioned above it should be pointed out that, in general, anomalous rotatory dispersion is caused by the superposition of normal rotations of opposite sign and unequal dispersion. These rotations may have their origin either in the same molecule or in different molecules (Lowry, 1935). Anomalous rotatory dispersion is shown by a solution

made by mixing two colourless liquids with opposite rotatory power and unequal dispersion (Biot, 1836), but such a solution does not show the Cotton effect. For the Cotton effect to appear, the two rotations must have their origin in the same molecule; furthermore the rotatory dispersion must be anomalous in the region of an absorption band originating in the optically active molecules. A solution of sugar coloured with magenta, for example, does not show the Cotton effect (Cotton, 1895).

The Cotton Effect in Diamagnetic Nickel Complexes.

Pfeiffer and his collaborators relied on rotatory dispersion measurements alone to detect the Cotton effect. It is clear from what has been said above that their dispersion studies need supplementing with absorption measurements before the existence of the Cotton effect can be considered as established. Moreover, it is necessary to show that the bands in which the Cotton effect occurs are due to the presence of the metal atom in the molecule. The author has therefore studied the absorption of several of the metal complexes in the visible region by means of a Hilger-Nutting spectrophotometer.

The absorption spectra for two nickel complexes, viz. (*a*) bis-formylcamphor-ethylenediimine-nickel (IX), (*b*) bis - salicylaldehyde - propylene-diimine-nickel (I) are shown in Figs. 5 and 6 respectively. Absorption measurements were made on optically inactive compounds, but this introduces no difficulties since, as Brode and Adams have shown (1925), optical enantiomorphs are characterised by identical absorption spectra. From Fig. 5 it can be seen that the dispersion curve crosses the axis of zero rotation at a wave length very close to that of the maximum of the absorption band. The dispersion data for bis-salicylaldehyde-d-propylene-diimine-nickel (see Fig. 6)[5] were not continued sufficiently far towards the ultra-violet to allow the dispersion curve to cut the axis of zero rotation, but a rough extrapolation showed that it would most likely do so in the neighbourhood of 4,500 Å., which represents a distance of 450 Å. from the head of the absorption band at 4,050 Å. Differences of this order, between band head and wave length for zero rotation have been observed by Mathieu (1936) in his study of the Cotton effect among cobaltic ammines.

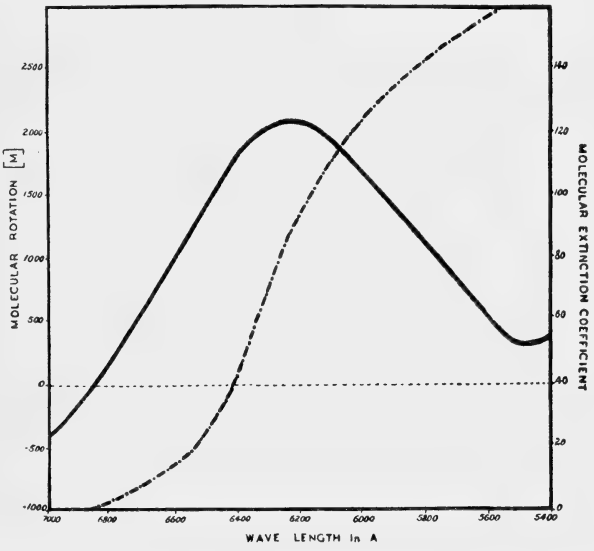

Fig. V.—Ethylene-diimine-formyl-camphor-nickel 0·0086 M in methyl alcohol.

Absorption ————
Rotatory dispersion —·—·—·— (data from Pfeiffer's paper).

There are several important features to be noted in Figs. 5 and 6. In the former, the band with a maximum at 6,200 Å. is definitely due to the presence

[5] I am indebted to Dr. J. E. Mills for permission to publish the data relating to the ultra-violet region in this diagram. These data form part of a joint investigation of the absorption spectra of para- and diamagnetic nickel complexes, a short account of which is shortly to appear in *J. Amer. Chem. Soc.*

of nickel, since the colourless metal-free compound shows no absorption in this region. The Cotton effect for bis-formylcamphor-ethylenediimine-nickel (IX) (Fig. 5) therefore, occurs in a band[6] which arises from the presence of the nickel atom in the molecule. This is an important point, since, as will be shown later, a metal complex may show the Cotton effect in a band not necessarily due to the presence of a metal atom.

The effect of introducing a nickel atom into bis-salicylaldehyde propylenediimine is clearly shown in Fig. 6, where the curve on the extreme right represents the absorption of the metal-free compound, while the curve adjacent to it represents the absorption of the metal containing compound. The band with a maximum at 4,050 Å. is clearly associated with the presence of the metal atom. In neither bis-salicylaldehyde-propylenediimine nor its nickel compound are there any bands in the visible region comparable in strength with those of the violet and ultra-violet. It will be noted that the strong band of bis-salicylaldehyde-ethylenediimine (I) with a maximum at 3,200 Å. is shifted to the red (to 3,400 Å.) in the metal compound.

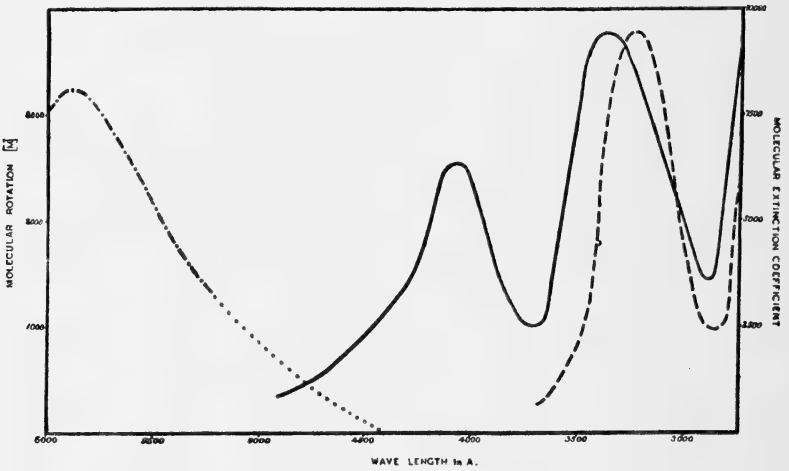

Fig. VI.—Propylenediimine-bis-salicylaldehyde-nickel.
0· M in ethyl alcohol.
Absorption ——— Rotatory dispersion —·—·—·—· (Pfieffer).
Propylenediimine-bis-salicylaldehyde absorption — — — —

The combined dispersion and absorption measurements show that both compounds (I) and (IX) show the Cotton effect, notwithstanding the fact that, being diamagnetic, they both contain square coordinated nickel. Some explanation other than that which postulates the existence of tetrahedrally coordinated nickel must therefore be sought to account for the appearance of the effect.

At the outset it must be stated that it always seemed inherently improbable that the mere presence of an asymmetric carbon atom in a compound like bis-salicylaldehyde-*d*-propylenediimine-nickel should cause the nickel to change from square to tetrahedral coordination as suggested by Pfeiffer *et al.* (1938). There is no difficulty in accounting for the optical behaviour of this and related compounds in another way.

Some years ago Lowry and Walker (1933) put forward the view that " chromophoric groups can exhibit ' induced asymmetry ' as a result of which

[6] The band at 6,200 Å. is not the only one which can be attributed to the nickel atom; another and much stronger one occurs at 3,850 Å.

they themselves become optically active when coupled sufficiently closely to an asymmetric complex." This hypothesis was based upon the observation that " the dispersion equations of camphor and its derivatives are haunted by a low frequency term the period of which is definitely characteristic of the ketonic group ". In order to account for the occurrence of the Cotton effect among the planar (diamagnetic) complexes of nickel, it is suggested that the chromophoric nickel atom exhibits " induced asymmetry " when linked to an asymmetric chelate group, in the same manner as the ketonic group in camphor derivatives. As will be indicated in a later section, it seems essential that nickel be bound to the asymmetric chelate group by covalent bonds, if the Cotton effect is to appear.

A similar explanation can be given in regard to the appearance of the Cotton effect in the covalent complexes of Cu^{II} and Co^{II}, although it should be pointed out that evidence for the planar configuration in the complexes of these two metals, especially the latter, is not so complete as it is for nickel. From the arguments already outlined, however, there is strong indirect evidence for the planar distribution of bonds about copper (Cu^{II}) and for this reason absorption measurements were extended to the compounds bis - formylcamphor - ethylenediimine - copper (X) (Fig. 7) and bis - salicylaldehyde - propylenediimine - copper (III). From Fig. 7 it can be seen that the former compound has an absorption band the maximum of which is in the close neighbourhood of the point where the dispersion curve cuts the axis of zero rotation. Owing to the slight solubility of (III), molecular extinction coefficients for this compound could not be satisfactorily determined. Measurements on supersaturated solutions, however, show that the substance possesses a band with a maximum at 5,650 Å., whereas, from the rotary dispersion curve, a maximum would be expected in the neighbourhood of 5,700 Å. It is clear, then, that these two copper compounds also show the Cotton effect notwithstanding the fact that there is a planar distribution of bonds about the copper atoms.

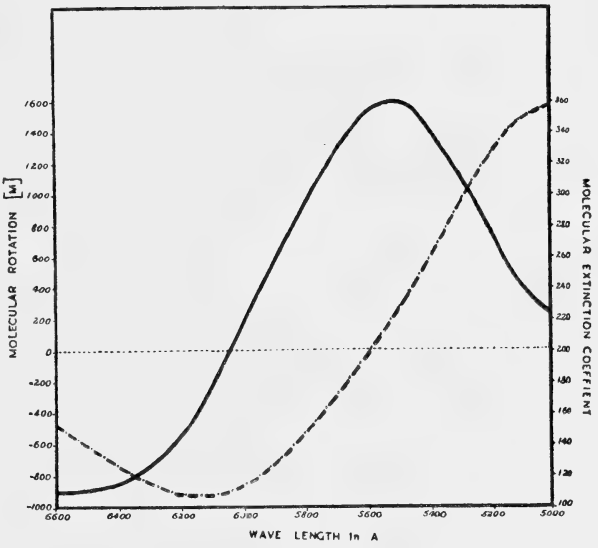

Fig. VII.—Ethylene-diimine-bis-formyl-camphor-copper. 0·00147 M in isobutyl alcohol.

Absorption ———
Rotation —·—·—·— (data from Pfeiffer's paper).

The Cotton Effect In Paramagnetic Nickel Complexes.

While most of the compounds described by Pfeiffer *et al.* (1938) showed anomalous rotatory dispersion in the visible spectrum, there were one or two notable exceptions, e.g. bis-formylcamphor-nickel (V). This compound shows no Cotton effect in the visible region of the spectrum (Pfeiffer *et al.*, 1938). It is not surprising, therefore that the absorption of a dilute (0·006 M.) alcoholic solution showed no marked absorption bands in the region 7,000 Å. to 4,300 Å.—

at least, no bands with intensities comparable to those of bands due to the presence of the nickel atom in covalent complexes. In this respect nickel-formylcamphor solution resembles aqueous solutions of paramagnetic nickel compounds containing hydrated or ammoniated nickel ions which show only bands of very small molecular extinction ($\varepsilon = 10$) (Ley, 1927, and Bjerrum, 1941). Bis-formylcamphor-nickel (V) has also been reexamined by French and Corbett (1940), who have extended both absorption and dispersion measurements well into the ultra-violet. These authors record a band maximum at 3,172 Å. and also a rotatory dispersion curve which crosses the axis of zero rotation at about this point. On the basis of this observation French and Corbett conclude that in (V), nickel is tetrahedrally coordinated. While the compound shows the Cotton effect, it is by no means certain that the band in which the effect appears is one which can be attributed to the presence of the nickel atom.

Thus formylcamphor itself has a band, the maximum of which is at about 2,630 Å. and a second band with a maximum at less than 2,400 Å. (Lowry and Southgate, 1910). In sodium formylcamphor the former of these bands appears to be shifted so that the maximum is at 3,000 Å., while the position of the second band (in the sodium salt) cannot be fixed from the published data. The 3,172 Å. band observed by French and Corbett for bis-formylcamphor-nickel may well be a band due to formylcamphor itself shifted from its position at 2,630 Å. by the presence of the ionically bound nickel in much the same way as it is shifted to 3,000 Å. by ionically bound sodium. In view of the uncertainty of the origin of the 3,172 Å. band and also the fact that square (diamagnetic) complexes show the Cotton effect, it is clear that the optical studies of bis-formylcamphor-nickel (V) so far, reveal nothing about the orientation of bonds about the nickel atom in this compound.

The Cotton Effect and Bond Type.

There is some evidence that occurrence of anomalous rotatory dispersion among metallic complexes is related to the nature of the metal to non-metal bonds occurring therein. The nickel-oxygen bonds in bis-formylcamphor are predominantly ionic and, from certain regularities already noted in magnetic studies of nickel compounds, the same may be said of the nickel-oxygen bonds in bis-benzoylcamphor nickel which, like the formyl complex, shows normal rotatory dispersion in the visible region. In this connection it is interesting to note some observations made by Lifschitz (1923) on closely related cobalt compounds. Lifschitz states that bis-formylcamphor-cobalt (Co^{II}) shows no Cotton effect. On the other hand the tris cobaltic compound does show the Cotton effect. Magnetic measurements indicate that in the cobaltous compound the Co–O bonds are predominantly ionic (see Table I), while in the cobaltic compound the corresponding bonds are covalent. Other instances could be quoted to show that the Cotton effect is absent in ionic metal complexes.[7] The whole question of the appearance or non-appearance of the Cotton effect is closely tied up with the differences between the absorption spectra of ionic and covalent[7] metal complexes. The two ionic complexes which fail to show anomalous rotatory dispersion in the visible region, viz. the nickel and cobaltous compounds of formylcamphor, also fail to show any absorption bands in that region—at least any bands of intensity comparable with that found at 6,200 Å. in diamagnetic bis-formylcamphor-ethylenediimine-nickel (Fig. 5).

The Usefulness of the Cotton Effect in Stereochemical Studies.

It would be premature to generalise at this stage, but as far as the metal compounds studied in this paper are concerned, it appears that the manifestation

[7] The terms ionic and-or covalent here refer to the metal–non-metal bonds.

of the Cotton effect does not depend on the orientation of valence bonds about the chromophoric metal atom but on the character of these bonds, that is whether they are predominantly covalent or ionic.[8] Bond character may determine bond orientation, as in the case of the nickel atom and in so far as this is true, the Cotton effect may be useful in determining structure. There are, however, indications that the determination of bond character may be achieved by a study of absorption spectra alone. Definite differences have already been noted in the absorption spectra of certain dia- and paramagnetic complexes of nickel[5] and in the limited field so far explored, bond type and orientation can be determined without recourse to the more difficult measurements of rotatory dispersion.

Acknowledgments.

The author is indebted to Mr. G. K. Hughes for specimens of formyl-camphor, to Dr. R. Lemberg and the Council for National Health and Medical Research for the use of the Hilger-Nutting spectrophotometer, to Mr. J. McInnes for assistance in preparing the diagrams for this paper, and lastly to the Australian Commonwealth Government for a grant to purchase an electromagnet for the magnetic work.

Summary.

Magnetic susceptibility measurements are used to determine the orientation and character of the bonds uniting metal atoms to various organic molecules. It is shown that the certain square coordinated complexes of nickel and copper exhibit the Cotton effect in bands due to the presence of the metal atom. The Cotton effect is attributed to the fact that the chromophoric metal atoms exhibit "induced asymmetry" when linked to asymmetric chelate groups. The possibility of using Cotton effect studies to determine the character and orientation of chemical bonds is briefly discussed.

References.

Biot, M.: *C.R. Acad. Sc.*, Paris, 1836, *2*, 543.
Beevers, C. A., and Lipson, H.: *Proc. Roy. Soc.*, 1934, (A), *146*, 570.
Bjerrum, J.: 1941 Dissertation, Copenhagen.
Bose, D. M., and Datta, S.: *Nature*, 1931, *128*, 725.
Brasseur, H., and de Rassenfosse, A.: *Bull. Soc. Min. France*, 1938, LXI, 129.
Brode, W. R., and Adams, R.: *J. Amer. Chem. Soc.*, 1924, *46*, 2032.
Bruhat, M. G.: *C.R. Acad. Sci.*, Paris, 1930, *47*, 251.
Chrobak, L.: *Z. Krist.*, 1934, *88*, 35.
Cotton, A.: *C.R. Acad. Sci.*, Paris, 1895, *120*, 989, 1044.
Cox, E. G., Sharatt, E., Wardlaw, W., and Webster, K. C.: *J. Chem. Soc.*, 1936, 129.
Cox, E. G., and Webster, K. C.: *J. Chem. Soc.*, 1935, 731.
Cox, E. G., Wardlaw, W., and Webster, K. C.: *J. Chem. Soc.*, 1935, 1475.
Ebert, F.: *Z. anorg. allg. Chem.*, 1931, *193*, 395.
Elliott, N.: Dissertation, Calif. Inst. Technology, Pasadena, Calif., U.S.A., 1938.
French, H. S., and Corbett, G.: *J. Amer. Chem. Soc.*, 1940, *62*, 3219.
Harker, D.: *Z. Krist.*, 1936, *93*, 136.
Jensen, K. A.: *Z. anorg. allgm. Chem.*, 1936, *229*, 265.
Johnson, C. H.: *Trans. Faraday Soc.*, 1932, *28*, 845.
Ley: *Z. anorg. allgm. Chem.*, 1927, *164*, 395.
Lifschitz, J.: *Z. Phys. Chem.*, 1923, *105*, 27.
Lowry, T. M., and Southgate, H. W.: *J. Chem. Soc.*, 1910, *97*, 905.
Lowry, T. M., and Walker: *Nature*, 1933, *131*, 566.
Lowry, T. M.: Optical Rotatory Power, Longman, Green, London, 1935.
Mathieu, J. P.: *Bull. Soc. Chim. France*, 1930, *47*, 251.
Mathieu, J. P.: *Bull. Soc. Chim. France*, 1936, Ser. 5, *3*, 477.

[8] It is interesting to note that Raman spectra may also be used to discriminate between ionic and covalent bonding in metal complexes. Of the two complexes, ionic $[Co(NH_3)_6]^{++}$ and covalent $[Co(NH_3)_6]^{+++}$ only the second gives Raman lines attributable to the Co–N bonds (Bose and Datta, 1931).

Mellor, D. P., and Quodling, F. M. : This Journal, 1936, LXX, 205.
Mellor, D. P., and Lockwood, W. H. : *Nature*, 1940, *145*, 862 ; This Journal, 1940, LXX, IV, 141.
Mellor, D. P. : *Aust. J. Sc.*, 1941, *3*, 99.
Pauling, L. : *J. Amer. Chem. Soc.*, 1931, *53*, 1367.
Pauling, L., and Huggins, M. : *Z. Krist.*, 1934, *87*, 205.
Pauling, L. : The Nature of the Chemical Bond, Cornell University Press, Ithaca, New York, 1940.
Peyronel, G. : *Z. Krist.*, 1941, *103*, 157.
Pfeiffer, P., Christelheit, W., Hesse, T., Pfitzner, H., and Thielert, H. : *J. prakt. Chem.*, 1938, *150*, 261.
Porter, C. R. : *J. Chem. Soc.*, 1938, 368.
Sugden, S. : *J. Chem. Soc.*, 1932, 246a.
Sugden, S. : *J. Chem. Soc.*, 1932, 161b.
Takagi and Ishiwara : Sc. Rep. Tôhoku Imp. Univ., Ser. I, Maths. Phys. and Chem., 1914, *3*, 127.
Tschugaeff, L. : *J. Russ. Phys. Chem. Soc.*, 1910, *42*, 1466.
Tunnell, G., Posnjak, E., and Ksanda, C. J. : *Z. Krist.*, 1935, *90*, 120.
Twyman, F., and Allsopp, C. B. : The Practice of Absorption Spectrophotometry, Adam Hilger, London, 1934.

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ON THE FREQUENCY OF THE PRIMES.

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Communicated by Professor H. S. Carslaw.

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k, m, n denote integers, p denotes primes. J. S. Broderick[1] recently proved a theorem, equivalent to that of Chebyshev on the distribution of primes, by methods which involve only the elementary properties of the integers. Instead of the transcendental function $\log n$ he uses the numerical function

$$\lambda(n)=\sum_{\nu=1}^{n}\frac{1}{\nu}, \tag{1}$$

and proves that the number $\pi(n)$ of primes not exceeding n satisfies the inequality,

$$\frac{1}{20}<\pi(n)\frac{\lambda(n)}{n}<14 \qquad (n\geq 2) \tag{2}$$

Simplifying Broderick's proof I obtained[2] the better estimate

$$\frac{1}{8}<\pi(n)\frac{\lambda(n)}{n}<12 \qquad (n\geq 2)* \tag{3}$$

Following up more rigorously the lines of my proof, I show in this paper that

$$\frac{1}{2}<\pi(n)\frac{\lambda(n)}{n}<3 \qquad (n\geq 2) \tag{4}$$

This estimate is easily deduced from the formula

$$\mu(2^n)-\frac{\lambda(n)}{n}<\pi(n)\frac{\lambda(n)}{n}<2\mu(2^n)+\frac{10}{\lambda(n)} \qquad (n\geq 2) \tag{5}$$

where

$$\mu(n)=\sum_{\nu=1}^{n}\frac{(-1)^{\nu-1}}{\nu} \tag{6}$$

which means that, for large n,

$$\mu-\varepsilon<\pi(n)\frac{\lambda(n)}{n}<2\mu+\varepsilon, \tag{7}$$

where

$$\mu=\lim_{n\to\infty}\mu(n)\ [=\log 2]. \tag{8}$$

(7) corresponds to the well-known result

$$\log 2\leq\liminf\ \pi(n)\ \frac{\log n}{n}\leq\limsup\ \pi(n)\ \frac{\log n}{n}\leq 2\log 2. \tag{9}$$

1. *Estimates for* $\lambda(n)$ *and* $\mu(n)$.

$$\lambda(n)+\lambda(m)-1\leq\lambda(nm)<\lambda(n)+\lambda(m) \qquad (n\geq 1,\ m\geq 1).[1] \tag{10}$$

Proof: The left hand inequality holds for $n=1$ and $m\geq 1$. Using induction,

$$\lambda((n+1)m)=\lambda(nm)+\frac{1}{nm+1}+\ldots.+\frac{1}{nm+m}$$

$$\geq\lambda(n)+\lambda(m)-1+\frac{m}{nm+m}=\lambda(n+1)+\lambda(m)-1.$$

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* By a slight alteration of the proof the sharper inequality $\frac{1}{8}<\pi(n)\frac{\lambda(n)}{n}<6$ can be obtained.

On the other hand,

$$\lambda(nm)=\left(1+\frac{1}{2}+..+\frac{1}{n}\right)+\left(\frac{1}{n+1}+..+\frac{1}{2n}\right)+..+\left(\frac{1}{(m-1)n+1}+..+\frac{1}{mn}\right)$$
$$<\lambda(n)+1+\frac{1}{2}+..+\frac{1}{m-1}<\lambda(n)+\lambda(m).$$

By repeated application of (10), it follows that

(11) $$k(\lambda(n)-1)+1\leq\lambda(n^k)\leq k\lambda(n) \qquad (n\geq 1,\ k\geq 1),$$

whence, for $n=2$,

(12) $$\frac{k}{2}+1\leq\lambda(2^k)\leq\frac{3k}{2} \qquad (k\geq 1)$$

As $$\lambda(2^k)=1+\frac{1}{2}+\left(\frac{1}{3}+\frac{1}{4}\right)+..+\left(\frac{1}{2^{k-1}+1}+..+\frac{1}{2^k}\right)$$

(12) can be sharpened to

(12′) $$\frac{1}{2}k+1\leq\lambda(2^k)\leq k+1 \qquad (k\geq 0).$$

Another estimate for $\lambda(2^k)$ can be obtained by using the identity

(13) $$\lambda(2n)=\lambda(n)+\mu(2n) \qquad (n\geq 1);$$

we have

$$\lambda(2^k)=\mu(2^k)+\mu(2^{k-1})+..+\mu(2)+1,$$

hence, as $\mu(2n)$ is increasing with n,

$$\lambda(2^k)\leq k\mu(2^k)+1 \qquad (k\geq 0).$$

On the other hand, as $\mu(2m-1)>\mu(2n)$ $\qquad (m\geq 1,\ n\geq 1)$,

$$\lambda(2^k)=\mu(2^k)+\left(\mu(2^{k-1}-1)-\frac{1}{2^{k-1}}\right)+..+\left(\mu(2-1)-\frac{1}{2}\right)+1$$
$$>k\mu(2^k)+1-\frac{1}{2}-\frac{1}{4}-..-\frac{1}{2^{k-1}}>k\mu(2^k) \qquad (k\geq 0);$$

thus

(12″) $$k\mu(2^k)<\lambda(2^k)\leq k\mu(2^k)+1 \qquad (k\geq 0).$$

It is easily calculated that $\mu(25)<\frac{5}{7}$ and $\mu(20)>\frac{2}{3}$, hence

(14) $$\mu(2n)<\frac{5}{7}<\frac{3}{4} \qquad (n\geq 1),$$

(15) $$\mu(2n)>\frac{2}{3} \qquad (n\geq 10).$$

It should also be noted that

(16) $$\frac{\lambda(m)}{m}>\frac{\lambda(n)}{n} \text{ for } m<n.$$

2. *Estimate for* $\pi(n)$.

We have

(17) $$\prod_{n<p\leq 2n} p \;\Big|\; \binom{2n}{n}=\frac{(2n)!}{n!\ n!} \;\Big|\; \prod_{p^r\leq 2n<p^{r+1}} p^r \qquad (n\geq 1),$$

since (i) the primes with $n<p\leq 2n$ divide $(2n)!$ but not $n!$; and (ii) p divides $\binom{2n}{n}$ to the power

$$\sum_{s=1}^{r}\left(\left[\frac{2n}{p^s}\right]-2\left[\frac{n}{p^s}\right]\right)\leq r$$

each element of the sum being ≤ 1.

Hence

$$n^{\pi(2n)-\pi(n)} < \prod_{n<p\leq 2n} p \leq \binom{2n}{n} \leq \prod_{p\leq 2n} p^r \leq (2n)^{\pi(2n)} \qquad (n\geq 1). \tag{18}$$

Now

$$\frac{2^{2n}}{2n} \leq \binom{2n}{n} \leq 2^{2n} \qquad (n\geq 1); \tag{19}$$

for

$$\binom{2n}{n} = 2^n \frac{1\,.\,3\,.\,5\,\ldots\,.\,(2n-1)}{1\,.\,2\,.\,3\,\ldots\,.\,n} \leq 2^{2n}$$

and

$$\binom{2n}{n} = 2^n \frac{3\,.\,5\,.\,\ldots\,.\,(2n-1)}{1\,.\,2\,.\,\ldots\,.\,n-1} \cdot \frac{1}{n} \geqq 2^{2n-1} \cdot \frac{1}{n} = \frac{2^{2n}}{2n}$$

By (18) and (19)

$$2^{2n} \leq (2n)^{\pi(2n)+1} \qquad (n\geq 1) \tag{20}$$

$$n^{\pi(2n)-\pi(n)} < 2^{2n} \qquad (n\geq 1).* \tag{21}$$

3. *Lower bound for* $\pi(n)$.

Let $n=2m$; then, by (12''), (20) and (11),

$$2m\mu(2^{2m}) < \lambda(2^{2m}) \leq \lambda((2m)^{\pi(2m)+1}) \leq (\pi(2m)+1)\lambda(2m) \qquad (m\geq 1), \tag{22}$$

i.e.,

$$\pi(2m)\frac{\lambda(2m)}{2m} > \mu(2^{2m}) - \frac{\lambda(2m)}{2m}. \tag{23}$$

Also, for $n=(2m-1)$, $\pi(2m-1)=\pi(2m)$, whence, using (16) and (23),

$$\pi(2m-1)\frac{\lambda(2m-1)}{2m-1} > \pi(2m)\frac{\lambda(2m)}{2m} > \mu(2^{2m}) - \frac{\lambda(2m)}{2m} > \mu(2^{2m-1}) - \frac{\lambda(2m-1)}{2m-1} \qquad (m\geq 2). \tag{24}$$

By (23) and (24),

$$\pi(n)\frac{\lambda(n)}{n} > \mu(2^n) - \frac{\lambda(n)}{n} \qquad (n\geq 2). \tag{25}$$

4. *Upper bound for* $\pi(n)$.

$$\pi(n)\frac{\lambda(n)}{n} < 2\mu(2^n) + \frac{10}{\lambda(n)} \qquad (n\geq 2). \tag{26}$$

Proof:

(i) $2\leq n\leq 8$:

$$\pi(n)\frac{\lambda(n)}{n} < \pi(8)\frac{\lambda(2)}{2} = 4\frac{3}{4} = 3,$$

$$2\mu(2^n) + \frac{10}{\lambda(n)} > \frac{10}{\lambda(8)} \geq \frac{10}{3\mu(8)+1} > \frac{10}{3\,.\,\frac{3}{4}+1} = \frac{40}{13} > 3,$$

using (16), (12'') and (14).

(ii) $8\leq n\leq 16$:

$$\pi(n)\frac{\lambda(n)}{n} < \pi(16)\frac{\lambda(8)}{8} < 6\frac{3\mu(8)+1}{8} < 6\frac{3\,.\,\frac{3}{4}+1}{8} = \frac{39}{16},$$

$$2\mu(2^n) + \frac{10}{\lambda(n)} > \frac{10}{\lambda(16)} \geq \frac{10}{4\mu(16)+1} > \frac{10}{4\,.\,\frac{3}{4}+1} = \frac{5}{2} > \frac{39}{16}.$$

(iii) $16\leq n\leq 32$:

$$\pi(n)\frac{\lambda(n)}{n} < \pi(32)\frac{\lambda(16)}{16} < 11\frac{4\mu(16)+1}{16} < 11\frac{4\,.\,\frac{3}{4}+1}{16} = \frac{11}{4},$$

$$2\mu(2^n) + \frac{10}{\lambda(n)} > \frac{4}{3} + \frac{10}{\lambda(32)} \geq \frac{4}{3} + \frac{10}{5\mu(32)+1} > \frac{4}{3} + \frac{10}{5\,.\,\frac{3}{4}+1} = \frac{4}{3} + \frac{40}{19} > 3 > \frac{11}{4}.$$

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* For (17), (18), (21) compare, e.g., the proof of Theorem 112 in Landau's *Zahlentheorie*.

(iv) $32 \leq n \leq 64$: $\pi(n)\frac{\lambda(n)}{n} < \pi(64)\frac{\lambda(32)}{32} < 18\frac{5\mu(32)+1}{32} < 18\frac{5 \cdot \frac{5}{7}+1}{32} = \frac{18}{7}$,

$$2\mu(2^n)+\frac{10}{\lambda(n)} > \frac{4}{3}+\frac{10}{\lambda(64)} \geq \frac{4}{3}+\frac{10}{6\mu(64)+1} > \frac{4}{3}+\frac{10}{6 \cdot \frac{3}{4}+1} = \frac{4}{3}+\frac{20}{11} > \frac{18}{7}.$$

(v) $64 \leq n \leq 128$: $\pi(n)\frac{\lambda(n)}{n} < \pi(128)\frac{\lambda(64)}{64} \leq 31\frac{6\mu(64)+1}{64} < 32\frac{6 \cdot \frac{3}{4}+1}{64} = \frac{11}{4}$

$$2\mu(2^n)+\frac{10}{\lambda(n)} > \frac{4}{3}+\frac{10}{\lambda(128)} > \frac{4}{3}+\frac{10}{7\mu(128)+1} > \frac{4}{3}+\frac{10}{7 \cdot \frac{5}{7}+1} = 3 > \frac{11}{4}.$$

(vi) $n = 2m \geq 128$:

Proof by induction : by (11), (21), (12''),

(27) $$(\pi(2m)-\pi(m))(\lambda(m)-1) < \lambda(m^{\pi(2m)-\pi(m)}) < \lambda(2^{2m}) \leq 2m\mu(2^{2m})+1,$$

whence

(28) $$\pi(2m) < \frac{2m\mu(2^{2m})+1}{\lambda(m)-1}+\pi(m),$$

i.e., by (13),

(29) $$\pi(2m)\frac{\lambda(2m)}{2m} < \frac{\lambda(2m)}{\lambda(m)-1}\left(\mu(2^{2m})+\frac{1}{2m}\right)+\pi(m)\frac{\lambda(m)}{m} \cdot \frac{\lambda(2m)}{2\lambda(m)}$$

$$< \mu(2^{2m})+\frac{1}{\lambda(m)-1}\left(\mu(2^{2m})(\mu(2m)+1)+\frac{\lambda(2m)}{2m}\right)+\left(2\mu(2^m)+\frac{10}{\lambda(m)}\right)\frac{\lambda(2m)}{2\lambda(m)}$$

$$= \mu(2^{2m})+\frac{1}{\lambda(m)-1}\left(\mu(2^{2m})(\mu(2m)+1)+\frac{\lambda(2m)}{2m}\right)$$

$$+\mu(2^m)+\frac{1}{\lambda(m)}\left(\mu(2^m)\mu(2m)+5\frac{\lambda(2m)}{\lambda(m)}\right)$$

$$< 2\mu(2^{2m})+\frac{1}{\lambda(2m)}\left\{\frac{\lambda(2m)}{\lambda(m)-1}\left(\mu(2^{2m})(\mu(2m)+1)+\frac{\lambda(2m)}{2m}\right)\right.$$

$$\left.+\frac{\lambda(2m)}{\lambda(m)}\left(\mu(2^m)\mu(2m)+5\frac{\lambda(2m)}{\lambda(m)}\right)\right\}$$

Now,

(30) $$\frac{\lambda(2m)}{\lambda(m)-1} = 1+\frac{\mu(2m)+1}{\lambda(m)-1} < 1+\frac{\frac{5}{7}+1}{\lambda(64)-1} < 1+\frac{\frac{5}{7}+1}{6\mu(64)-1} < 1+\frac{\frac{5}{7}+1}{6 \cdot \frac{2}{3}-1} = \frac{11}{7}$$

(31) $$\frac{\lambda(2m)}{\lambda(m)} = 1+\frac{\mu(2m)}{\lambda(m)} < 1+\frac{\frac{5}{7}}{\lambda(64)} < 1+\frac{\frac{5}{7}}{6\mu(64)} < 1+\frac{\frac{5}{7}}{6 \cdot \frac{2}{3}} = \frac{33}{28},$$

(32) $$\frac{\lambda(2m)}{2m} < \frac{\lambda(128)}{128} < \frac{7\mu(128)+1}{128} < \frac{7 \cdot \frac{5}{7}+1}{128} = \frac{3}{64},$$

whence,

(33) $$\{\ldots.\} < \frac{11}{7}\left(\frac{5}{7} \cdot \frac{12}{7}+\frac{3}{64}\right)+\frac{33}{28}\left(\frac{5}{7} \cdot \frac{5}{7}+5\frac{33}{28}\right) < 10-\frac{1}{3}$$

By (29) and (33),

$$\pi(2m)\frac{\lambda(2m)}{2m}<2\mu(2^{2m})+\frac{10-\frac{1}{3}}{\lambda(2m)}<2\mu(2^{2m})+\frac{10}{\lambda(2m)} \tag{34}$$

(vii) $n=2m+1>128$:

$$\begin{aligned}\pi(2m+1)\frac{\lambda(2m+1)}{2m+1}&\leq(\pi(2m)+1)\frac{\lambda(2m+1)}{2m+1}<\pi(2m)\frac{\lambda(2m)}{2m}+\frac{\lambda(2m+1)}{2m+1}\\&<2\mu(2^{2m})+\frac{10-\frac{1}{3}}{\lambda(2m)}+\frac{\lambda(2m+1)}{2m+1}\\&<2\mu(2^{2m+1})+\frac{1}{\lambda(2m+1)}\left\{\left(10-\frac{1}{3}\right)\frac{\lambda(2m+1)}{\lambda(2m)}+\frac{\lambda(2m+1)^2}{2m+1}\right\}\end{aligned} \tag{35}$$

Now,

$$\frac{\lambda(2m+1)}{\lambda(2m)}=1+\frac{1}{(2m+1)\lambda(2m)}<1+\frac{1}{129\lambda(128)}<1+\frac{1}{129\ .\ 7\mu(128)}<1+\frac{1}{129\ .\ 7\ .\ \frac{2}{3}}$$

$$=1+\frac{1}{602}, \tag{36}$$

$$\frac{\lambda(2m+1)^2}{2m+1}<\frac{\lambda(128)^2}{128}<\frac{(7\mu(128)+1)^2}{128}<\frac{\left(7\ .\ \frac{5}{7}+1\right)^2}{128}=\frac{36}{128}=\frac{9}{32}. \tag{37}$$

By (36), (37),

$$\{\ldots.\}<\left(10-\frac{1}{3}\right)\left(1+\frac{1}{602}\right)+\frac{9}{32}<10-\frac{1}{3}+\frac{1}{60}+\frac{9}{32}<10, \tag{38}$$

hence, from (35),

$$\pi(2m+1)\frac{\lambda(2m+1)}{2m+1}<2\mu(2^{2m+1})+\frac{10}{\lambda(2m+1)}. \tag{39}$$

This proves (26) for all $n\geq 2$. (25) and (26) establish (5).

5. *Proof of* (4).

By (i)-(v)

$$\pi(n)\frac{\lambda(n)}{n}<3 \text{ for } 2\leq n\leq 128. \tag{40}$$

Also, $128\leq n\leq 256$:

$$\pi(n)\frac{\lambda(n)}{n}<\pi(256)\frac{\lambda(128)}{128}<54\frac{7\mu(128)+1}{128}<54\frac{7\ .\ \frac{5}{7}+1}{128}=\frac{81}{32}<3,$$

$256\leq n\leq 512$:

$$\pi(n)\frac{\lambda(n)}{n}<\pi(512)\frac{\lambda(256)}{256}<97\frac{8\mu(256)+1}{256}<100\frac{8\ .\ \frac{5}{7}+1}{250}<\frac{14}{5}<3,$$

$512\leq n\leq 1024$:

$$\pi(n)\frac{\lambda(n)}{n}<\pi(1024)\frac{\lambda(512)}{512}<172\frac{9\mu(512)+1}{512}<172\frac{9\ .\ \frac{5}{7}+1}{512}=\frac{172\ .\ 52}{512\ .\ 7}<3;$$

and for $n \geq 1024$, by (26),

$$\pi(n)\frac{\lambda(n)}{n} < 2\mu(2^n) + \frac{10}{\lambda(n)} < \frac{10}{7} + \frac{10}{\lambda(1024)}$$
$$< \frac{10}{7} + \frac{10}{10\mu(1024)} < \frac{10}{7} + \frac{1}{2} = \frac{10}{7} + \frac{3}{2} < 3.$$

Thus, (40) holds for all $n \geq 2$.

On the other hand,

$$\pi(2)\frac{\lambda(2)}{2} = \frac{3}{4} > \frac{1}{2},$$

$$\pi(3)\frac{\lambda(3)}{3} > \pi(4)\frac{\lambda(4)}{4} = 2 \cdot \frac{25}{48} > \frac{1}{2},$$

$5 \leq n \leq 8$: $$\pi(n)\frac{\lambda(n)}{n} > \pi(5)\frac{\lambda(8)}{8} = 3 \cdot \frac{761}{8 \cdot 280} > \frac{1}{2}$$

$9 \leq n \leq 16$: $$\pi(n)\frac{\lambda(n)}{n} > \pi(9) \cdot \frac{\lambda(16)}{16} > 4 \cdot \frac{3}{16} > \frac{1}{2},$$

$17 \leq n \leq 32$: $$\pi(n)\frac{\lambda(n)}{n} > \pi(17) \cdot \frac{\lambda(32)}{32} > 7 \cdot \frac{1+\frac{5}{2}}{32} = \frac{49}{64} > \frac{1}{2},$$

and for $n \geq 32$, by (25),

$$\pi(n)\frac{\lambda(n)}{n} > \mu(2^n) - \frac{\lambda(n)}{n} > \frac{2}{3} - \frac{\lambda(32)}{32} > \frac{2}{3} - \frac{5 \cdot \frac{5}{7} + 1}{32} = \frac{2}{3} - \frac{1}{7} = \frac{11}{21} > \frac{1}{2}.$$

Hence

$$\pi(n)\frac{\lambda(n)}{n} > \frac{1}{2} \qquad (n \geq 2) \tag{41}$$

(40) and (41) establish (4).

References.

(1) *Journal London Math. Soc.*, 1939, *14*, 303-310.
(2) *Journal London Math. Soc.*, 1940, *15*, 257-259.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales

April 2, 1941.

The Annual Meeting, being the five hundred and eighty-fifth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. Eighty-five members were present. The minutes of the general monthly meeting of December 4, 1940, were read and confirmed.

The following gentlemen were elected officers and members of the Council for the coming year:

President:

D. P. MELLOR, M.Sc.

Vice-Presidents:

H. S. HALCRO WARDLAW, D.Sc., F.A.C.I.
W. L. WATERHOUSE, M.C., D.Sc.Agr., D.I.C., F.L.S.
E. H. BOOTH, M.C., D.Sc., F.Inst.P.
PROF. T. G. ROOM, M.A.

Honorary Secretaries:

PROF. A. P. ELKIN, M.A., Ph.D.
C. ANDERSON, M.A., D.Sc.

Honorary Treasurer:

A. R. PENFOLD, F.A.C.I., F.C.S.

Members of Council:

PROF. V. A. BAILEY, M.A., D.Phil., F.Inst.P.
A. BOLLIGER, Ph.D., A.A.C.I.
G. H. BRIGGS, B.Sc., Ph.D., F.Inst.P.
IDA A. BROWN, D.Sc.
W. R. BROWNE, D.Sc.
PROF. C. E. FAWSITT, D.Sc., Ph.D.
E. J. KENNY, M.Aust.I.M.M.
W. H. MAZE, M.Sc.
G. D. OSBORNE, D.Sc., Ph.D.
A. CLUNIES ROSS, B.Sc., F.C.A. (Aust.).

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and on the motion of Mr. M. B. Welch, seconded by Mr. R. H. Goddard, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 28th FEBRUARY, 1941.

LIABILITIES.

1940. £		£ s. d.	£ s. d.	1941. £ s. d.
	Trust Funds—			
	Clarke Memorial Fund—			
	Balance as at 29th February, 1940 ..	1,715 14 7		
	Add Interest for year ended 28th February, 1941	68 12 7		
		£1,784 7 2		
	Less Expenses in connection with 1940 Lecture—			
	Printing .. £3 13 2			
	Advertising .. 0 15 0			
		4 8 2		
			1,779 19 0	
	Walter Burfitt Prize Fund—			
	Balance as at 29th February, 1940 ..	661 17 9		
	Add Interest for year ended 28th February, 1941	26 9 6		
			688 7 3	
	Liversidge Bequest—			
	Balance as at 29th February, 1940 ..	703 9 8		
	Add Interest for year ended 28th February, 1941	28 2 10		
		£731 12 6		
	Less Expenses in connection with 1940 Lecture—			
	Lecture Fee .. £42 0 0			
	Printing .. 2 13 8			
	Advertising .. 0 17 6			
		45 11 2		
			686 1 4	
3,081				3,154 7 7
10	Subscriptions Paid in Advance			15 15 0
156	Provision for Unexpired Proportion of Life Membership Subscriptions			124 0 0
26,686	Accumulated Fund			27,204 17 5
£29,933				£30,499 0 0

ASSETS.

1940. £		£ s. d.	1941. £ s. d.
	Cash at Bank and on Hand—		
	The Union Bank of Australia Ltd.	48 9 10	
	Commonwealth Savings Bank of Australia	48 9 5	
	Petty Cash	3 15 7	
214			100 14 10
	Bonds and Inscribed Stock—		
	Bonds (Face Value £1,600)	1,611 5 0	
	Stock (Face Value £6,860)	6,827 11 3	
7,839			8,438 16 3
	Science House Management Committee—		
14,590	Payments to date		14,650 0 0
	Sundry Debtors—		
	Subscriptions Unpaid	197 12 10	
—	*Less* Reserve	197 12 10	
6,800	Library		6,800 0 0
	Furniture	454 9 9	
	Less Depreciation written off	20 11 5	
411			433 18 4
	Pictures	43 15 8	
	Less Depreciation written off	2 3 9	
44			41 11 11
	Microscopes	19 8 8	
	Less Depreciation written off	0 19 6	
19			18 9 2
	Lantern	16 6 0	
	Less Depreciation written off	0 16 6	
16			15 9 6
£29,933			£30,499 0 0

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1941, as disclosed thereby. We have obtained certificates showing that the whole of the Bonds and Inscribed Stock are held by the Society's bankers for safe keeping.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 18th March, 1941.

(Sgd.) M. B. WELCH.
Hon. Treasurer.

REVENUE ACCOUNT FOR THE YEAR ENDED 28th FEBRUARY, 1941.

Year ended 29th Feb., 1940.			Year ended 28th February, 1941.		
£	£		£ s. d.	£	s. d.
4		To Advertising	3 6 9		
30		„ Cleaning	32 2 6		
26		„ Depreciation	24 11 2		
6		„ Electric Light and Gas	9 8 2		
14		„ Insurance	14 6 1		
77		„ Library Maintenance	39 12 6		
56		„ Miscellaneous Expenses	54 11 10		
259		„ Office Salaries and Audit Fees	283 19 6		
29		„ Office Sundries and Stationery	16 6 7		
119		„ Printing	115 4 7		
273		„ Printing and Publishing Journal	362 4 6		
6		„ Repairs	4 13 2		
49		„ Stamps and Telegrams	50 19 4		
17		„ Telephone	18 14 9		
		„ Annual Dinner—			
55		Expenses	£34 19 8		
41	14	*Less* Received	29 8 0		
			5 11 8		
	979			1,035	13 1
		„ Balance, being Net Revenue for the Year, transferred			
	50	to Accumulated Fund		443	7 4
	£1,029			£1,479	0 5

Year ended 29th Feb., 1940.			Year ended 28th February, 1941.		
£	£		£ s. d.	£	s. d.
	476	By Members' Subscriptions		531	6 0
	—	„ Government Subsidy		400	0 0
260		„ Science House Receipts	275 0 0		
16		*Less* Rent Paid	41 16 2		
—	244			233	3 10
	100	„ Miscellaneous Receipts		98	9 3
297		„ Interest Received	307 6 3		
		Less—			
		Clarke Memorial Fund	£68 12 7		
		Walter Burfitt Prize Fund	26 9 6		
120		Liversidge Bequest	28 2 10		
			123 4 11		
—	177			184	1 4
	32	„ Proportion of Life Members' Subscriptions		32	0 0
	£1,029			£1,479	0 5

ACCUMULATED FUND ACCOUNT FOR THE YEAR ENDED 28th FEBRUARY, 1941.

1941—February 28—	£	s.	d.
To Arrears of Subscriptions, written off	119	1	0
„ Balance Carried Down	27,204	17	5
	£27,323	18	5

1940—February 29—	£	s.	d.
By Balance from last Account	26,685	15	1
1941—February 28—			
By Amount transferred from Bad Debts Reserve Account	134	16	0
„ Science House Capital Account—Adjustment	60	0	0
„ Net Revenue for the Year	443	7	4
	£27,323	18	5
1941—February 28—			
By Balance Brought Down	£27,204	17	5

The Annual Report of the Council (1940-41) was read, and on the motion of Mr. A. R. Penfold, seconded by Mr. A. D. Ollé, was adopted.

Report of the Council (Rule XXVI), 1940-1941.

We regret to report the loss by death of eight members since April 1st, 1940: Mr. Frank Leverrier (1909), Mr. Henry H. Baker (1919), Mr. John Farrell (1910), Mr. John Patrick O'Neill (1932), Mr. Thomas Lindsay Willan (1921), Mr. Edmund Cooper Manfred (1880), Mr. James Nangle (1893), and Mr. George Henry Blakemore (1905).

By resignation the Society has lost seven members: S. W. E. Parsons, Victor Marcus Coppleson, Frank Hambridge, Charles Vicars Potts, Elizabeth F. Lawrence, William Charles Wentworth, Percy Ash.

Six members were written off the register of members.

Sixty-two ordinary members were elected during the year.

Annual Dinner.—In conformity with the precedent established during the World War of 1914-1918, it was resolved that the Annual Dinner should not be held during the present war.

During the year beginning April 1st, there have been nine general meetings and ten Council meetings. The average attendance at general meetings was 53, and at Council meetings 14.

Forty papers were read before the Society during 1940. The following short talks were given also:

"Highlights of a Recent World Tour," by Mr. A. R. Penfold.
"Submarine Canyons," by Dr. G. D. Osborne.
"The Early History of Wireless," by Mr. G. G. Blake.

Exhibits were shown by Professor A. P. Elkin and Mr. A. R. Penfold, whose "glass textiles" created great interest.

Four Popular Science Lectures were given in the winter months, and all were very well attended both by members of the Society and the general public.

July 18.—"An Inland People of New Guinea," by Phyllis M. Kaberry, M.A., Ph.D.
August 15.—"Insects and Disease in War-time, with Special Reference to Mosquito Biology," by A. R. Woodhill, B.Sc.Agr.
September 19—"Energy for Living," by R. N. Robertson, B.Sc., Ph.D.
October 17.—"Romances of Chemistry—Coal Stockings and Glass Ties," by A. R. Penfold, F.A.C.I., F.C.S.

Symposium.—A very successful symposium on "Potassium" was held during the general monthly meeting of August. The speakers were as follows:

C. de Vahl Davis, B.Sc.Agr.: "The Commercial Potash Situation in Australia."
D. P. Mellor, M.Sc.: "Some Aspects of the Chemistry of Potassium, with special reference to Potential Sources in Australia."
N. H. Parbery, D.Sc.: "Potassium in Soil."
R. N. Robertson, B.Sc., Ph.D. (*vice* Professor E. Ashby): "Potassium in Plants."

Mr. de Vahl Davis also showed a film entitled "The Mining and Manufacture of Potash in Europe." There was an attendance of 106 at the symposium, and the addresses delivered were later printed in pamphlet form for distribution to members and others who were interested.

Clarke Memorial Lecture.—The Clarke Memorial Lecture was delivered on June 14th, by Mr. E. J. Kenny, and was entitled " The Geologist and Sub-surface Water."

Liversidge Research Lecture.—The third Liversidge Research Lecture to be given under the auspices of the Royal Society was delivered on October 31st, by Mr. G. J. Burrows, B.Sc., and was entitled " Organic Arsenicals in Peace and War."

Finance.—The finances of the Society as shown by the balance sheet are in a satisfactory condition. On the advice of the Finance Committee, an amount of £600 was invested in the Commonwealth War Loan during 1940.

Government Grant.—The Government of New South Wales made a grant of £400 to the Royal Society of New South Wales for the year 1940.

Science House.—The Royal Society has been represented on the Science House Management Committee by Mr. E. Cheel, who was appointed Secretary-Treasurer of the Committee, and by Mr. M. B. Welch, with Dr. C. Anderson and Dr. H. S. H. Wardlaw as substitute representatives.

The Society's share of the profits on Science House has been of the same order as that of the past two or three years.

Paper Rationing.—In response to representations made by its officers, the Royal Society was granted exemption from the proposed rationing of paper adopted as a war economy by the Department of Trade and Customs. The Department, in granting the exemption, asked that economy in paper should be observed, as far as was consistent with the publication of papers on research.

Alteration of Rules.—An alteration was made to Rule VIII. Other alterations, concerning a proposed postal ballot, were referred to a committee.

Members on Active Service.—It was resolved to remit for the duration of the war the subscriptions of any members of the Society on active service with His Majesty's Forces.

The Library.

Exchanges.—The number of societies and institutions with which publications are exchanged has declined considerably owing to the entry of more countries into the war, or their occupation by the enemy. The present number of exchange societies and institutions is 268. Since the war began, 97 exchanges in all have been removed from the exchange lists, including societies and institutions in Germany, Italy, France, Belgium, the Netherlands, Norway, and Rumania.

Accessions.—Owing also to war conditions the number of accessions has decreased by about one-quarter since the war began, namely from 3,317 for the year ended March, 1939, to 2,348 for the year ending March, 1941.

Borrowers and Readers.—The number of readers who visited the library during the year was thirty-three, and sixty-three periodicals were borrowed by members and accredited readers. Periodicals were sent out on loan to the following societies and institutions: The University of Sydney (Fisher Library, Geological Library and Botany School), the C.S.I.R. (Division of Plant Industry, Canberra, the McMaster Laboratory, Sydney, and the Food Preservation Laboratory, Homebush), the British Medical Association, Sydney, the Broken Hill Proprietary Ltd., Newcastle, the Standards Association, the Australian Institute for International Affairs, Sydney, the University of Western Australia, the Royal Society of Tasmania, and the Irrigation Commission, Sydney.

Bookbinding and Purchase of Periodicals.—A number of periodicals have been bound at a cost of £8 11s. 6d. Periodicals have been purchased at a cost of £31 1s., the total amount for binding and purchase of books being £39 12s. 6d.

Furniture and Fittings.—The portion of the library used as a reading room has been greatly improved in several ways. The floor has been covered with linoleum, and a carpet has been provided under the reading table. Comfortable chairs have been obtained, and a powerful new light for reading has been installed over the table.

Shelving.—There is still considerable crowding on the shelves, and it is hoped to be able to dispose of a number of duplicates, which are now occupying valuable shelf space.

A. P. ELKIN,
President.

The following donations were received: 798 parts of periodicals, and 32 whole volumes.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The President announced that the Clarke Memorial Lecture for 1941 would be given by Mr. C. A. Sussmilch, the title of the lecture being " The Climate of Australia in Past Ages."

The President announced that the Clarke Memorial Medal for 1941 had been awarded to Professor F. Wood Jones, of the University of Manchester, England.

Format of the Journal and Proceedings.—It was announced that the Council was considering an alteration in the format of the Journal and Proceedings, to quarto size, in order to effect an economy in cost and in the amount of paper used, and also to bring the journal into line with other present-day journals. After discussion it was unanimously decided that the format be altered to quarto size.

Election of Auditor.—On the motion of Mr. A. R. Penfold, seconded by Mr. E. Cheel, Messrs. Horley & Horley were reappointed as the Society's auditors for the year 1941-1942.

The President, Professor A. P. Elkin, delivered his address, entitled " Science, Society and ' Everyman '."

Professor A. P. Elkin, the retiring President, then installed Mr. D. P. Mellor, M.Sc., as President for the year 1941-1942, and the latter expressed his thanks and his pleasure on taking office. On behalf of the members Dr. W. R. Browne expressed appreciation of the work of the retiring President, and of his interesting address. Professor Elkin briefly replied.

Notice of Motion.—Mr. M. B. Welch moved

" That the Council be requested to appoint a committee to consider revision of the Society's Rules."

May 7, 1941.

The five hundred and eighty-sixth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, President, was in the chair. Thirty-one members and five visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Max Charles Cohen, Harold Theodore Clyde Howard, Dansie Thomas Sawkins, and Thomas Baikie Swanson.

Popular Science Lectures.—It was announced that the following lectures had been arranged for 1941 :

June 19th.—" Some Aspects of Hydatid Disease in Australia," by Professor H. Dew, M.B., B.S., F.R.C.S.
July 17th.—" The Modern Aeroplane," by Professor A. V. Stephens, M.A.
August 21st.—" War and the Fisheries," by H. Thompson, M.A., D.Sc.
September 18th.—" Weighing the Stars," by R. van der R. Woolley, M.Sc., Ph.D.
October 16th.—" The Cow, the Chemist and Ourselves—The Nutrition of Farm Animals in Plenty and in Drought," by E. G. Hallsworth, B.Sc., Ph.D. (Leeds).

It was announced that the Clarke Memorial Lecture would be given by Mr. Sussmilch on May 22nd.

The following donations were received : 154 parts of periodicals, and 14 whole volumes.

Revision of Rules.—It was announced that a committee had been appointed to continue with the revision of the rules.

The following papers were read :

" Progressive Rates of Tax in Australia," Professor H. S. Carslaw.
" The Effect of the Synthetic Oestrogens, Stilboestrol and Hexoestrol on the Pouch and Scrotum of *Trichosurus vulpecula*," by A. Bolliger, Ph.D., and A. J. Canny, M.B., Ch.M.
" Magnetic Studies of Co-ordination Compounds. Part V. Binuclear Derivatives of Diphenyl Methyl Arsine," by D. P. Mellor, M.Sc., and D. P. Craig.

Lecturette.—A lecturette on " Fiji and the Fijians " was given by Dr. Arthur Capell, M.A.

June 4, 1941.

The five hundred and eighty-seventh General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Mr. R. W. Challinor, a past President, was in the chair. Thirty-two members and five visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The following donations were received : 186 parts of periodicals and 11 whole volumes.

The following papers were read :

" The Jurassic Fishes of N.S.W.," by R. T. Wade, M.A., Ph.D.
" An Examination of the Essential Oils Distilled from the Tips and Normal Cut of *Eucalyptus polybractea*," by Philip A. Berry, M.Sc., and Thomas B. Swanson, M.Sc.

Films.—By courtesy of the Rural Bank of New South Wales, two films were shown :

" The Menace of Soil Erosion."
" The Red Terror."

July 2, 1941.

The five hundred and eighty-eighth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, President, was in the chair. Twenty-seven members and two visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for election as an ordinary member of the Society was read for the second time. The following person was duly elected as an ordinary member of the Society: Irvine Armstrong Watson.

The following donations were received: 195 parts of periodicals, and 15 whole volumes.

The following paper was presented by Professor T. G. Room, in the absence of the author:

"Elementary Remarks on Goodness of Fit of Hypotheses and Pearson's χ^2 Test," by D. T. Sawkins, M.A.

Lecturette.—A lecturette on the "Mineral Resources of the Great Powers in Relation to the International Situation" was given by Dr. G. D. Osborne.

Exhibit.—An exhibit of "Some Recent Developments in Plastics" was shown by Mr. F. R. Morrison.

August 6, 1941.

The five hundred and eighty-ninth General Monthly Meeting, held in the Hall of Science House, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, President, was in the chair. Thirty-seven members and three visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time.

The following persons were duly elected as ordinary members of the Society: Samuel Raymond Brown and David Parker Craig.

The following donations were received: 158 parts of periodicals and 10 whole volumes.

The following papers were read:

"Permian Blastoids from New South Wales," by Ida A. Brown, D.Sc.

"Bryozoa from the Silurian and Devonian of New South Wales," by Miss Joan Crockford, B.Sc.

Lecturettes.—The following lecturettes were given:

"A Scale of Magnitudes," by Dr. F. Lions.

"The Electron Microscope," by Dr. R. E. B. Makinson.

September 3, 1941.

The five hundred and ninetieth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, President, was in the chair. Twenty-nine members were present. The minutes of the preceding meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The following donations were received: 196 parts of periodicals, and 13 whole volumes.

The following papers were read:

"A Note on Determinations of Physiological Specialization in Flax Rust," by W. L. Waterhouse, D.Sc.Agr., D.I.C., F.L.S., and I. A. Watson, Ph.D., B.Sc.Agr.

"The Thiamine (Vitamin B_1) Content of the Urine of *Trichosurus vulpecula*," by A. Bolliger, Ph.D., and C. R. Austin, B.Sc.

"The Chemistry of Bivalent and Trivalent Rhodium: Hexacovalent Complexes of Rhodous Halides with Diphenylmethylarsine," by F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc.

Lecturette.—"Vitamin B_1—its Discovery and Importance in Nutrition and Disease," by Dr. A. Bolliger.

October 1, 1941.

The five hundred and ninety-first General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, President, was in the chair. Thirty-four members and one visitor were present. The minutes of the preceding meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time, and the following was duly elected as an ordinary member: George Livingstone Melville.

The following donations were received : 130 parts of periodicals, and 3 whole volumes.

The following papers were read by title :

" Radial Heat Flow in Circular Cylinders with a General Boundary Condition. Part II," by J. C. Jaeger. (Communicated by Professor H. S. Carslaw.)

" The Chemistry of Bivalent and Trivalent Rhodium : A Qualitative Study of the Effect of Reducing Agents on Trivalent Rhodium Salts ; and the Properties of Some Rhodous Salts," by F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc.

Symposium.—A symposium on Light Metals was held.

Aluminium, magnesium and other light metals are assuming ever-increasing importance in modern industry, particularly in aeroplane construction. It was decided, therefore, to devote the October general meeting to a Symposium on the Light Metals.

The following were the subjects and speakers :

1. The Sources of the Light Metals, by Professor L. A. Cotton.
2. The Manufacture of and Demand for the Light Metals, by Dr. J. E. Mills.
3. Some Alloys of the Light Metals, by Miss V. Suvoroff, B.Sc.

November 5, 1941.

The five hundred and ninety-second General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, President, was in the chair. Thirty-three members and two visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

Guide to Authors.—The President drew attention to the " Guide to Authors " which has recently been published by the Society.

The following donations were received : 185 parts of periodicals and 2 whole volumes.

The following papers were read :

" The Chemistry of Bivalent and Trivalent Rhodium : Compounds of Rhodic Halides with Tertiary Arsines," by F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc.

" Studies on the Cultivation of the Tung Oil Tree, *Aleurites Fordii*. Part II. Study of a Heavy Yield of Fruit Obtained on the North Coast of N.S.W.," by A. R. Penfold, F.A.C.I., F.C.S., F. R. Morrison, A.A.C.I., F.C.S., and S. Smith-White, B.Sc.Agr.

" The Stereochemistry of Some Metallic Complexes with Special Reference to their Magnetic Properties and the Cotton Effect," by D. P. Mellor, M.Sc.

" Triassic Fishes of N.S.W.," by R. T. Wade, M.A., Ph.D.

Exhibits.—The following exhibits were shown :

The Jelley-Leitz Refractometer, by Dr. G. D. Osborne.

A Fluorescent Chromatographic Column, by Mr. A. J. Tow.

December 3, 1941.

The five hundred and ninety-third General Monthly Meeting of the Society was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, President, was in the chair. Thirty-four members and two visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time.

The following persons were duly elected as ordinary members of the Society : Victor le Roy Alldis, Matthew John Morrissey, and Victoria Suvoroff.

Walter Burfitt Prize.—The President announced that the Walter Burfitt Prize for 1941 had been awarded to Dr. Frederick W. Whitehouse, Lecturer in Geology in the University of Queensland, and at present a member of the A.I.F., for his work on the Geology of Queensland, in particular the Geology of Western Queensland and researches on the Cambrian trilobites.

The following donations were received : 167 parts of periodicals, and 5 whole volumes.

The following paper was read by title :

" On the Frequency of the Primes," by Dr. F. A. Behrend. (Communicated by Professor H. S. Carslaw.)

Lecturette.—" The Sulphanilamide Drugs," by Dr. F. Lions.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Dr. W. R. Browne.

Secretary : H. O. Fletcher.

Eight meetings were held during the year, the average attendance being sixteen members and eight visitors.

April 18th.—Exhibits : By Mr. J. A. Dulhunty : (*a*) Torbanites, consisting mainly of algal remains, from Rylstone, N.S.W. ; (*b*) A specimen of Tasmanite made up of plant material = Cannel Coal ; (*c*) Tasmanite, made up of spores ; (*d*) New Zealand oil shale made up of macerated vascular plant material ; (*e*) A specimen of original torbanite, from Torbane Hill, Scotland ; (*f*) " Oil-shale " from Queensland—Cannel Coal of Jurassic age ; (*g*) " Oil-shale," vascular plant canneloid sapropel of Jurassic age from New South Wales ; (*h*) " Algal Cannel." Algal and vascular plant sapropel. Capertee Valley, N.S.W. Mr. Lambeth recorded the discovery of a new horizon of torbanite 20-25 miles west of Mittagong. The outcrop is 1 mile 1 chain in length, and 14 inches thick. There are 30-40% volatile hydrocarbons. By Mr. T. Hodge-Smith : The Moorleah Aerolite, the first stony meteorite recorded from Tasmania. By Dr. Ida Brown : (*a*) Calyx of a crinoid, *Tribrachiocrinus*, with some of the arms attached to the dorsal cup, from the Upper Marine beds at Black Head, Gerrringong ; (*b*) A blastoid, *Indoblastus* ? sp. nov., from the Fenestella beds of the Permian ; (*c*) A brittle-star, *Sturtzura* ? *brisingoides* (Gregory), from Silurian slates at Euchareena, N.S.W. By Miss Quodling : (*a*) A specimen of selenite showing dehydration ellipses, produced by placing a hot point on the surface of the crystal ; (*b*) A lead box for use in the cobalt nitrate staining process for distinguishing felspars ; (*c*) Microphotographs and slides showing staining of the felspars by the cobalt nitrate process. By Mr. Waterhouse : (*a*) A well crystallised specimen of manganhedenbergite, from the southern end of No. 10 level, Zinc Corporation Mine, Broken Hill ; (*b*) Arborescent native copper found in a cavity in gossan, Mt. Isa, Queensland. By Dr. W. R. Browne : Rock fragments of Devonian quartzite found in surface soil at Hay, N.S.W. Locally termed " cherts." By Mr. Fletcher : (*a*) A new gastropod from the Upper Marine beds at Rylstone ; (*b*) Three specimens of *Martiniopsis subpentagonalis* and *M. inflata* from the Lower Productus limestones of the Salt Range. By Dr. W. R. Browne : A series of slides illustrating features of physiographical interest in the New South Wales highlands.

May 16th.—Address by Major C. T. Madigan, " Sand Dunes and Ridges."

June 20th.—Address by Mr. E. C. Andrews, " The Canyon of the Colorado."

July 18th.—Address by Mr. E. J. Kenny, " Some Ore-Deposits in N.S.W."

August 15th.—Address by Dr. W. G. Woolnough, " The Tectonic Relations between Continental Australia and Alpine Foldings in the East Indies."

September 19th.—Exhibits : By Professor Cotton : (*a*) Recent conglomerate cemented round an old bayonet : (*b*) Native copper with gold in a quartz reef ; (*c*) Suite of fossils, *Stutchburia*, *Astartila* and *Bellerophon* from the Carboniferous, 70 feet below the surface, east of Breeza, N.S.W. By Mr. Whitworth : (*a*) Dumortierite, Pershing County, Nevada, U.S.A. ; (*b*) Andalusite with crystallised pyrophyllite ; (*c*) Rich bauxite (60% Al_2O_3) from Trundle, N.S.W. ; (*d*) Garnet, from schist, 30 miles west of Broken Hill, N.S.W. ; (*e*) Tertiary leaf, Trunkey, N.S.W. ; (*f*) Set of specimens of Archæocyathinæ from Beltana, South Australia. By Dr. G. D. Osborne : The Dollar integrating micrometer for use in Rosiwal analysis. By Miss Crockford : Short discourse on fossil Bryozoa. By Dr. Ida Brown : *Martiniopsis subradiata* partly silicified, showing spiral supports replaced by chalcedony, revealed by careful etching and drilling. By Mr. Fletcher : Tertiary fossil shells from Miocene limestone, Tobruk, Libya. By Professor W. R. Browne : (*a*) Slides showing unconformity between the Permian and Devonian, Glen Davis-Capertee Road ; (*b*) Short account of coal seams in both the Upper Marine and Upper Coal Measures at Kanangra Walls, and of the fluvio-glacial conglomerates.

October 17th.—Address by Mr. C. St. J. Mulholland, " The Underground Water of the Sydney District."

December 5th.—Address by Dr. F. W. Whitehouse, " Geological Aspects of the Artesian Basin, Queensland."

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

INDUSTRY

Chairman : A. D. Ollé, F.C.S., A.A.C.I.

Visits were made during the year to the following :

1941.

May 13th.—Columbia Pencil and Crayon Co., McEvoy Street, Waterloo.

June 10th.—Dental Hospital, Chalmers Street, Sydney.

September 9th.—Stedman-Henderson's Sweets Ltd., Waterloo.

OBITUARY NOTICES.

Henry Herbert Baker, who joined the Royal Society in 1919, was born in 1868. Mr. Baker was chairman of directors of the firm of W. Watson and Son, which he had established in Australia more than 50 years ago. He was well known to the members of the medical and dental professions, and was closely connected with the development of X-rays in Australia and with all aspects of optical science. He was keenly interested in the Astronomical Society and was a member of it and of the Millions Club.

George Henry Blakemore, who died at the age of 73, was known in mining circles throughout Australia. At his death he was chairman of directors of Takuapa Valley Tin Dredging and Tartut Basin Tin Dredging Company. He was born at Copperfield, in North Queensland, his father having been also a prominent mining man. Mr. Blakemore began his career at Broken Hill as an assayer ; later he was manager of the Great Cobar Copper Mine, and then took charge of the old refinery at Lithgow. Some years later he began business as a private mining engineer. He leaves a widow and three sons.

Frank Leverrier, who became a member of the Royal Society in 1909, was born in Sydney in 1863, spent some of his early years in France, but returned to New South Wales, where he was educated at Fort Street Public School and the Sydney Grammar School. Proceeding to the University of Sydney, he graduated in Arts, in Law and in Science, and he chose to follow the legal profession. He was made a K.C. in 1911. In 1907 he was elected a Fellow of the Senate of the University ; was Challis Lecturer in Law ; from 1914 to 1917 and again in 1921 Mr. Leverrier was Vice-Chancellor of the University of Sydney.

Edmund Cooper Manfred, who had played a prominent part in the civic and business life of Goulburn for more than sixty years, died at Goulburn, aged 84 years. He was the father of M. E. Manfred, M.L.C., Assistant Minister. The only child of Mr. Edward Manfred, architect and surveyor, he was born at Kensington, London, on June 5, 1856. He qualified as an architect and began practice at Goulburn. He designed many of the town's best known buildings, and served on almost every public body in Goulburn. He was an early member of the Royal Society of N.S.W. and the Royal Historical Society of N.S.W. and was a Mason. He is survived by six sons.

James Nangle, who had been Government Astronomer for New South Wales for fifteen years, died on February 22, 1941, in his seventy-third year. He exerted an important influence in this State in the fields of architecture, education, and astronomy. He began practice as an architect late last century, several large buildings in Sydney being designed by him, and he specialised in school and church buildings. He was President of the Royal Australian Institute of Architects in the year 1936-37, and was elected a Fellow of the Royal Institute of British Architects in 1937. Several papers on the properties of Australian timbers and building stones were published by him in the Journal of the Royal Society of New South Wales, which he joined in 1893, and of which he was President in the year 1920-21.

While still in practice he undertook some teaching in architecture at Sydney Technical College, and this led to his important work in technical education. In 1913 he was appointed Superintendent of Technical Education. He reorganised the technical education courses, bringing the technical colleges into closer touch with industries and trades by setting up a series of advisory committees, on which the professions and trades as well as educational authorities were represented. Similar internal committees provided for coordination of effort by the administrative and teaching staffs. He always stressed that a good system of technical education must be coordinated with the industries it was to serve. During his administration the attendance at technical colleges in New South Wales rose from four thousand to fourteen thousand. While he was Superintendent of Technical Education in New South Wales, he paid extended visits to Western Australia and Tasmania to advise the governments of those States on the organisation of their technical education systems. He retired in 1934.

One important task undertaken by James Nangle was the supervision of the vocational training system for returned soldiers carried out by the Commonwealth Repatriation Department after the 1914-18 war. His services for this purpose were given by the Government of New South Wales to the Commonwealth Government, and altogether more than 20,000 returned soldiers who had been injured or whose training had been interrupted by active service were trained. He had to a marked degree the gift of the good administrator for obtaining cooperation and in making estimates of the absorptive capacities of the various trades and industries and in carrying out the training of the men he was very successful in getting support from the trade unions, technical colleges and universities. He was awarded the O.B.E. in 1920.

His interest in astronomy began early. He joined the New South Wales Branch of the British Astronomical Association in 1905, and was its president on many occasions, his ability as a speaker being an asset to the meetings. In 1908 he was elected a Fellow of the Royal Astronomical Society. He maintained an observatory at his residence in Marrickville until he became Government Astronomer in 1926, when the Observatory had a difficult period through which his administration steered it. James Nangle had at all times been most approachable and helpful to newcomers to the science of astronomy, and many have had their interest awakened by his numerous popular lectures and writings.

His friendliness and enthusiasm will be remembered by all who knew him. He is survived by his widow, daughter, and three sons.

John Patrick O'Neill joined the Society in 1932. Mr. O'Neill had for some time been chief timber expert for the Department of Railways of New South Wales.

Thomas Lindsay Willan, who joined the Society in 1921, was born in Sydney in 1895. He was educated at the Sydney High School, whence he entered the University of Sydney. He gained first-class honours and the University Medal for Geology at the B.Sc. examination. He entered the Geological Survey of N.S.W., and in 1924 left it to go to the Federated Malay States, where he was engaged until 1933 in survey work. Later he went to Burma, where he remained until his death from malaria towards the end of 1940.

INDEX.

A

Page.

Abstract of Proceedings xxi
Section of Geology xxx
Section of Industry xxxi
Alteration of Rules xxvi
Annual Dinner xxv
Annual Report and Balance Sheet .. xxii
Austin, C. R.—See Bolliger, A. .. 118
Authors, Notice to v
Awards of—
Clarke Memorial Medal xviii, xxvi
Liversidge Research Lectureship .. xx
Society's Medal and Money Prize .. xix
Walter Burfitt Prize xx

B

Behrend, F. A.—
On the Frequency of the Primes .. 169
Bequest, Form of v
Berry, P. A., and T. B. Swanson—
An Examination of the Essential Oils Distilled from the Tips and Normal Cut of *Eucalyptus polybractea* 65
Binuclear Copper Derivatives of Diphenyl Methyl Arsine 27
Blastoids, Permian, from New South Wales 96
Bolliger, A., and A. J. Canny—
The Effect of the Synthetic Œstrogens, Stilbœstrol and Hexœstrol on the Pouch and Scrotum of *Trichosurus vulpecula* 21
Bolliger, A., and C. R. Austin—
The Thiamin (Vitamin B_1) Content of the Urine of *Trichosurus vulpecula* 118
Brown, Ida A.—
Permian Blastoids from New South Wales 96
Bryozoa from the Silurian and Devonian of New South Wales 104
Burfitt Prize .. .. .. xx, xxix

C

Canny, A. J.—See Bolliger, A... .. 21
Carslaw, H. S.—
Progressive Rates of Tax in Australia 31
Clarke Memorial Fund xviii
Clarke Memorial Lecture .. ..
xviii, xxvi, xxvii, 47
Clarke Memorial Medal .. .. xviii, xxvi
Climate of Australia in Past Ages .. 47
Contents iii
Council, Report of the xxv

Page.

Craig, D. P.—See Mellor, D. P... .. 27
Crockford, Joan—
Bryozoa from the Silurian and Permian of New South Wales .. 104

D

Determinations of Physiological Specialisation in Flax Rust 115
Devonian and Silurian of New South Wales, Bryozoa from 104
Diphenyl Methyl Arsine, Binuclear Copper Derivatives of 27
Diphenylmethylarsine, Hexacovalent Complexes of Rhodous Halides with 127
Dwyer, F. P., and R. S. Nyholm—
The Chemistry of Bivalent and Trivalent Rhodium. Part I. A Qualitative Study of the Effect of Reducing Agents on Trivalent Rhodium Salts ; and the Properties of some Rhodous Salts 122
The Chemistry of Bivalent and Trivalent Rhodium. Part II. Hexacovalent Complexes of Rhodous Halides with Diphenylmethylarsine 127
The Chemistry of Bivalent and Trivalent Rhodium. Part III. Compounds of Rhodic Halides with Tertiary Arsines 140

E

Elkin, A. P.—
Presidential Address, " Science, Society and Everyman " 4
Essential Oils of *Eucalyptus polybractea*.. 65
Eucalyptus polybractea, Essential Oils of 65
Exhibits—
A Fluorescent Chromatographic Column xxix
The Jelley-Leitz Refractometer xxix
Some Recent Developments of Plastics xxviii

F

Films Shown xxvii
Finance xxvi
Fishes, The Jurassic, of New South Wales 71
Fishes, The Triassic, of New South Wales 144
Flax Rust, Determinations of Physiological Specialisation in .. 115

G

Page.
Goodness of Fit of Hypotheses and on Pearson's χ Test 85
Government Grant xxvi
Guide to Authors xxix

H

Hexacovalent Complexes of Rhodous Halides with Diphenylmethylarsine 127
Hexœstrol, Effects of on Pouch and Scrotum of *Trichosurus vulpecula* .. 21

J

Jaeger, J. C.—
Radial Heat Flow in Circular Cylinders with a General Boundary Condition 130
Journal and Proceedings, Alteration of Format xxvii
Jurassic Fishes of New South Wales .. 71

L

Lecturettes—
Fiji and the Fijians .. xxvii
Mineral Resources of the Great Powers in Relation to the International Situation xxviii
A Scale of Magnitudes .. xxviii
The Electron Microscope .. xxviii
Vitamin B_1, its Discovery and Importance in Nutrition and Disease xxviii
The Sulphanilamide Drugs .. xxix
Library xxvi
List of Members ix
Liversidge Research Lecture .. xx, xxvi

M

Magnetic Studies of Coordination Compounds. Part V. Binuclear Copper Derivatives of Diphenyl Methyl Arsine 27
Mellor, D. P., and D. P. Craig—
Magnetic Studies of Coordination Compounds. Part V. Binuclear Copper Derivatives of Diphenyl Methyl Arsine 27
Mellor, D. P.—
The Stereochemistry of some Metallic Complexes, with Special Reference to their Magnetic Properties and the Cotton Effect 157
Members on Active Service, Remission of Subscriptions by xxvi
Members, List of ix
Morrison, F. R.—See Penfold, A. R... 148

N

Page.
Nyholm, R. S.—See Dwyer, F. P. 122, 127, 140

O

Obituaries .. .. xvii, xxxi
Officers for 1941-1942 vii

P

Paper Rationing xxvi
Pearson's χ Test 85
Penfold, A. R., F. R. Morrison and S. Smith-White—
Studies on the Cultivation of the Tung Oil Tree, *Aleurites Fordii*. Part II. Study of a Heavy Yield of Fruit Obtained on the North Coast of New South Wales 148
Permian Blastoids from New South Wales 96
Physiological Specialisation in Flax Rust 115
Popular Science Lectures .. xxv, xxvii
Presidential Address by A. P. Elkin, "Science, Society, and Everyman" 4
Primes, On the Frequency of the .. 169
Progressive Rates of Tax in Australia .. 31
Publications vi

R

Radial Heat Flow in Circular Cylinders with a General Boundary Condition 130
Reducing Agents on Trivalent Rhodium Salts, Effects of 122
Report of the Council, 1940-1941 .. xxv
Rhodium, The Chemistry of Bivalent and Trivalent .. 122, 127, 140
Rhodous Halides, Hexacovalent Complexes of, with Diphenylmethylarsine 127
Rhodous Salts, Properties of Some .. 122

S

Sawkins, D. T.—
Remarks on Goodness of Fit of Hypotheses and on Pearson's χ Test 85
Science, Society, and Everyman—Presidential Address, by A. P. Elkin 4
Science House xxvi
Silurian and Devonian of New South Wales, Bryozoa from 104
Smith-White, S.—See Penfold, A. R... 148
Society's Medal and Money Prize .. xix
Stilbœstrol, Effect of, on Pouch and Scrotum of *Trichosurus vulpecula* .. 21
Sussmilch, C. A.—
The Climate of Australia in Past Ages (Clarke Memorial Lecture) .. 47

Page.
Swanson, T. B.—See Berry, P. A. .. 65
Symposia—
On Potassium xxv
On Light Metals xxix
Synthetic Œstrogens, Effect of, on the Pouch and Scrotum of *Trichosurus vulpecula* 21

T

Tax in Australia, Progressive Rates of.. 31
Thiamin (Vitamin B_1) Content of the Urine of *Trichosurus vulpecula* .. 118
Triassic Fishes of New South Wales.. 144
Trichosurus vulpecula, Effect of the Synthetic Œstrogens Stilbœstrol and Hexœstrol on the Pouch and Scrotum of 21
Page.
Trichosurus vulpecula, The Thiamin (Vitamin B_1) Content of the Urine of 118

W

Wade, R. T.—
The Jurassic Fishes of New South Wales 71
The Triassic Fishes of New South Wales 144
Walter Burfitt Prize; Awarded to Dr. F. W. Whitehouse .. xxix
Waterhouse, W. L., and I. A. Watson—
A Note on Determinations of Physiological Specialisation in Flax Rust 115
Watson, I. A.—See Waterhouse, W. L. 115

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OF NEW SOUTH WALES

FOR

1942

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CONTENTS

VOLUME LXXVI

Part I *

Page.

ART. I.—Presidential Address. By D. P. Mellor, M.Sc. (Issued September 21, 1942) .. 1

ART. II.—Methæmoglobin Formation. By John Williamson Legge, B.Sc. (Issued September 21, 1942) 47

ART. III.—A Note on the Essential Oil of *Eucalyptus conglobata* var. *anceps*. By P. A. Berry, M.Sc., and T. B. Swanson, M.Sc. (Issued August 12, 1942) 53

ART. IV.—Studies in Metamorphism and Assimilation in the Wellington District, N.S.W. II. The Dynamic and Contact Metamorphism of a Group of Ultrabasic Rocks. By Elizabeth M. Basnett, M.Sc. (Issued September 21, 1942) 55

ART. V.—The Tertiary Land Surface in Southern New England. By A. H. Voisey, M.Sc. (Issued September 21, 1942) 82

ART. VI.—Spermatorrhœa in Marsupials, with Special Reference to the Action of Sex Hormones on Spermatogenesis of *Trichosurus vulpecula*. By Adolph Bolliger, Ph.D. (Issued September 21, 1942) 86

ART. VII.—The Occurrence of Two Physiological Forms of *Leptospermum citratum* (Challinor, Cheel and Penfold) as Determined by Chemical Analysis of the Essential Oils. By A. R. Penfold, F.A.C.I., F.C.S., F. R. Morrison, A.A.C.I., F.C.S., and S. Smith-White, B.Sc.Agr. (Issued September 21, 1942) 93

Part II †

ART. VIII.—Clarke Memorial Lecture. The Heroic Period of Geological Work in Australia. By E. C. Andrews, B.A., F.G.S. (Issued November 6, 1942) .. 96

ART. IX.—The Chemistry of Bivalent and Trivalent Rhodium. Part IV. Polynuclear Complexes of Rhodium and Tin with Tertiary Arsines. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued November 6, 1942) 129

Part III ‡

ART. X.—The Chemistry of Bivalent and Trivalent Rhodium. Part V. Coordination Complexes of Rhodous Halides with Dialkyl Arsines. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued December 21, 1942) 133

ART. XI.—The Effect of Gonadotropin Obtained from Human Pregnancy Urine on the Pouch of *Trichosurus vulpecula*. By Adolph Bolliger, Ph.D. (Issued December 21, 1942) 137

ART. XII.—The Devonian Rugose Corals of the Tamworth District, N.S.W. By Dorothy Hill, Ph.D., D.Sc. (Issued December 21, 1942) 142

ART. XIII.—The Tamworth Series (Lower and Middle Devonian) near Attunga, N.S.W. By Ida A. Brown, D.Sc. (Issued December 21, 1942) 165

* Published October 15, 1942.

† Published November 23, 1942.

‡ Published May 26, 1943.

Page.

ART. XIV.—On Contact Transformations Associated with the Symplectic Group. By H. Schwerdtfeger. (Communicated by Professor H. S. Carslaw.) (Issued December 21, 1942) 177

ART. XV.—Middle Palæozoic Rugose Corals from the Wellington District, N.S.W. By Dorothy Hill, Ph.D., D.Sc. (Issued December 21, 1942) 182

ART. XVI.—Some Thermochemical Properties of the Torbanite of the Glen Davis Deposit. By R. F. Cane, M.Sc., A.A.C.I. (Issued December 21, 1942) 190

ART. XVII.—Moving Sources of Heat and the Temperature at Sliding Contacts. By J. C. Jaeger. (Issued April 2, 1943) 203

ART. XVIII.—A Method for the Estimation of Vegetable Material in Scoured Wool. By M. Lipson, B.Sc., A.A.C.I. (Issued April 2, 1943) 225

Part IV *

ART. XIX.—A Revision of Certain Species of Leptospermeæ. By Edwin Cheel. (Issued August 2, 1943) 229

ART. XX.—Physiography of the Wellington District, N.S.W. By Margaret J. Colditz, B.Sc. (Issued August 2, 1943) 235

ART. XXI.—Upper Ordovician Graptolite Horizons in the Yass-Jerrawa District, N.S.W. By Kathleen Sherrard, M.Sc. (Issued August 2, 1943) 252

ART. XXII.—Permian Bryozoa of Eastern Australia. Part III. Batostomellidæ and Fenestrellinidæ from Queensland, New South Wales, and Tasmania. By Joan M. Crockford, M.Sc. (Issued August 2, 1943) 258

ART. XXIII.—The Action of Solvents on Torbanite and the Nature of Extracted Products. By J. A. Dulhunty, B.Sc. (Issued August 2, 1943) 268

ART. XXIV.—The Chemistry of Bivalent and Trivalent Rhodium. Part VI. Pyridine Complexes of Rhodous Halides. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued August 2, 1943) 275

ART. XXV.—A Note on the Magnetic Behaviour of Potassium Cyanonickelite. By D. P. Mellor, M.Sc., and D. P. Craig, M.Sc. (Issued June 28, 1943) 281

ART. XXVI.—Functional Relations between Scrotum and Pouch and the Experimental Production of a Pouch-like Structure in the Male of *Trichosurus vulpecula*. By Adolph Bolliger, Ph.D. (Issued August 2, 1943).. 283

ART. XXVII.—Co-ordination Compounds Derived from Nicotinylacetone. By Francis Lions, B.Sc., Ph.D., Benjamin S. Morris, M.Sc., and Ernest Ritchie, M.Sc. (Issued September 1, 1943) 294

ART. XXVIII.—Progressive Rates of Tax in Australia. II. By H. S. Carslaw. (Issued September 1, 1943) 304

ART. XXIX.—Galileo and Newton : Their Times and Ours. By Professor O. U. Vonwiller. (Issued September 1, 1943).. 316

ART. XXX.—Chemistry of the Earth. By J. S. Anderson, Ph.D. (First Liversidge Lecture.) (Issued September 1, 1943) 329

ART. XXXI.—The Imperfect Crystal. By J. S. Anderson, Ph.D. (Second Liversidge Lecture.) (Issued September 1, 1943) 345

TITLE PAGE, CONTENTS, NOTICES, PUBLICATIONS i

OFFICERS FOR 1942-43 vii

LIST OF MEMBERS, AWARDS OF MEDALS, ETC. ix

ABSTRACT OF PROCEEDINGS xxi

PROCEEDINGS OF THE SECTION OF GEOLOGY xxxiv

INDEX TO VOLUME LXXVI xxxv

* Published December 17, 1943.

NOTICE.

The Royal Society of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

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Authors should submit their papers in typescript and in a condition ready for printing. All physico-chemical symbols and mathematical formulæ should be so clearly written that the compositor should find no difficulty in reading the manuscript. Sectional headings and tabular matter should not be underlined. Pen-illustrations accompanying papers should be made with black Indian ink upon smooth white Bristol board. Lettering and numbers should be such that, when the illustration or graph is reduced to 5 inches in width, the lettering will be quite legible. On graphs and text figures any lettering may be lightly inserted in pencil. Photo-micrographs should be rectangular rather than circular, to obviate too great a reduction. The size of a full page plate in the Journal is $5 \times 7\frac{3}{4}$ inches, and the general reduction of illustrations to this limit should be considered by authors. When drawings, etc., are submitted in a state unsuitable for reproduction, the cost of the preparation of such drawings for the process-block maker must be borne by the author. The cost of colouring plates or maps must also be borne by the author. Further particulars regarding the preparation of manuscripts are contained in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

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I bequeath the sum of £ to the Royal Society of New South Wales, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

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,,	XV	,,	,,	,,	,,	,,	1881,	,,	440,	,,
,,	XVI	,,	,,	,,	,,	,,	1882,	,,	327,	,,
,,	XVII	,,	,,	,,	,,	,,	1883,	,,	324,	,,
,,	XVIII	,,	,,	,,	,,	,,	1884,	,,	224,	,,
,,	XIX	,,	,,	,,	,,	,,	1885,	,,	240,	,,
,,	XX	,,	,,	,,	,,	,,	1886,	,,	396,	,,
,,	XXI	,,	,,	,,	,,	,,	1887,	,,	296,	,,
,,	XXII	,,	,,	,,	,,	,,	1888,	,,	390,	,,
,,	XXIII	,,	,,	,,	,,	,,	1889,	,,	534,	,,
,,	XXIV	,,	,,	,,	,,	,,	1890,	,,	290,	,,
,,	XXV	,,	,,	,,	,,	,,	1891,	,,	348,	,,
,,	XXVI	,,	,,	,,	,,	,,	1892,	,,	426,	,,
,,	XXVII	,,	,,	,,	,,	,,	1893,	,,	530,	,,
,,	XXVII	,,	,,	,,	,,	,,	1894,	,,	368,	,,
,,	XXIX	,,	,,	,,	,,	,,	1895,	,,	600,	,,
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,,	XXXII	,,	,,	,,	,,	,,	1898,	,,	476,	,,
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,,	XXXIV	,,	,,	,,	,,	,,	1900,	,,	484,	,,
,,	XXXV	,,	,,	,,	,,	,,	1901,	,,	581,	,,
,,	XXXVI	,,	,,	,,	,,	,,	1902,	,,	531,	,,
,,	XXXVII	,,	,,	,,	,,	,,	1903,	,,	663,	,,
,,	XXXVIII	,,	,,	,,	,,	,,	1904,	,,	604,	,,
,,	XXXIX	,,	,,	,,	,,	,,	1905,	,,	274,	,,
,,	XL	,,	,,	,,	,,	,,	1906,	,,	368,	,,
,,	XLI	,,	,,	,,	,,	,,	1907,	,,	377,	,,
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,,	XLVI	,,	,,	,,	,,	,,	1912,	,,	275,	,,
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,,	XLVIII	,,	,,	,,	,,	,,	1914,	,,	584,	,,
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,,	LI	,,	,,	,,	,,	,,	1917,	,,	786,	,,
,,	LII	,,	,,	,,	,,	,,	1918,	,,	624,	,,
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,,	LIV	,,	,,	,,	,,	,,	1920,	,,	312,	price £1 1s.
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,,	LVI	,,	,,	,,	,,	,,	1922,	,,	372,	,,
,,	LVII	,,	,,	,,	,,	,,	1923,	,,	421,	,,
,,	LVIII	,,	,,	,,	,,	,,	1924,	,,	366,	,,
,,	LIX	,,	,,	,,	,,	,,	1925,	,,	468,	,,
,,	LX	,,	,,	,,	,,	,,	1926,	,,	470,	,,
,,	LXI	,,	,,	,,	,,	,,	1927,	,,	492,	,,
,,	LXII	,,	,,	,,	,,	,,	1928,	,,	458,	,,
,,	LXIII	,,	,,	,,	,,	,,	1929,	,,	263,	,,
,,	LXIV	,,	,,	,,	,,	,,	1930,	,,	434,	,,
,,	LXV	,,	,,	,,	,,	,,	1931,	,,	366,	,,
,,	LXVI	,,	,,	,,	,,	,,	1932,	,,	601,	,,
,,	LXVII	,,	,,	,,	,,	,,	1933,	,,	511,	,,
,,	LXVIII	,,	,,	,,	,,	,,	1934,	,,	328,	,,
,,	LXIX	,,	,,	,,	,,	,,	1935,	,,	288,	,,
,,	LXX	,,	,,	,,	,,	,,	1936,	,,	528,	,,
,,	LXXI	,,	,,	,,	,,	,,	1937,	,,	708,	,,
,,	LXXII	,,	,,	,,	,,	,,	1938,	,,	396,	,,
,,	LXXIII	,,	,,	,,	,,	,,	1939,	,,	344,	,,
,,	LXXIV	,,	,,	,,	,,	,,	1940,	,,	658,	,,
,,	LXXV	,,	,,	,,	,,	,,	1941,	,,	224,	,,
,,	LXXVI	,,	,,	,,	,,	,,	1942,	,,	432,	,,

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* Resigned July 24, 1942.
† Elected July 24, 1942.
‡ Elected August 26, 1942.
|| Resigned August 26, 1942.

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as at March 1, 1943

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1935		‡Albert, Michel Francois, " Boomerang," Billyard-avenue, Elizabeth Bay.
1898		‡Alexander, Frank Lee, Surveyor, 67 Ocean-street, Woollahra.
1941		‡Alldis, Victor le Roy, L.S., Registered Surveyor, Young, N.S.W.
1905	P 3	Anderson, Charles, M.A., D.Sc. *Edin.*, C.M.Z.S., 17 Towns-road, Vaucluse. (President, 1924.)
1909	P 12	Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, " Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1930		Aston, Ronald Leslie, B.Sc., B.E. *Syd.*, M.Sc., Ph.D. *Cantab.*, A.M.I.E.Aust., Lecturer in Civil Engineering and Surveying in the University of Sydney ; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
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1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale ; p.r. 17 Thompson-street, Clifton Gardens.
1938		Black, Una Annie Frazer (Mrs.), B.Sc., 16 Melrose, Billyard-avenue, Elizabeth Bay.
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1933	P 21	Bolliger, Adolph, Ph.D., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney.
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1939	P 1	Bosworth, Richard Charles Leslie, M.Sc., D.Sc. *Adel.*, Ph.D. *Camb.*, F.A.C.I., F.Inst.P., c/o C.S.R. Co., Pyrmont ; p.r. 41 Spencer-road, Killara.
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1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney ; p.r. 19 Handley-avenue, Thornleigh.

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1942		Brown, Desmond J., B.Sc., 9 Agnes-street, Strathfield.
1935	P 3	Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.
1941		Brown, Samuel Raymond, A.C.A. *Aust.*, 87 Ashley-street, Chatswood.
1913	P 21	Browne, William Rowan, D.Sc., Reader in Geology in the University of Sydney. (President, 1932.)
1940		Buckley, Daphne M. (Mrs.), B.Sc., 4 Sharland-avenue, Chatswood.
1940		Buckley, Lindsay Arthur, B.Sc., 4 Sharland-avenue, Chatswood.
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. *Syd.*, F.R.A.C.S., "Radstoke," Elizabeth Bay.
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1940	P 1	Cane, Reginald Frank, M.Sc., A.A.C.I., National Oil Pty. Ltd., Glen Davis, N.S.W.
1940		Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
1938	P 2	‡Carey, Samuel Warren, D.Sc., Practising Petroleum Geologist, c/o Australasian Petroleum Co., Melbourne.
1903	P 5	Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
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1933		Chalmers, Robert Oliver, A.S.T.C., Assistant (Professional) in Mineralogy, Australian Museum, College-street, Sydney.
1940		Chambers, Maxwell Clark, B.Sc., c/o J. and E. Atkinson Pty. Ltd., 469-75 Kent-street, Sydney.
1913	P 20	Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
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1940		Clarke, Ronald Stuart, B.A., 28 Beecroft-road, Beecroft.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
1941		Cohen, Max Charles, B.Sc., No. 3, Explosives Factory, St Mary's, N.S.W.
1940		Cohen, Samuel Bernard, M.Sc., A.A.C.I., 24 Euroka-street, Northbridge.
1940	P 1	Colditz, Margaret Joyce, B.Sc., 9 Beach-street, Kogarah.
1940		Cole, Edward Ritchie, B.Sc., 14 Barwon-road, Lane Cove.
1940	P 1	Cole, Joyce Marie, B.Sc., 14 Barwon-road, Lane Cove.
1940		Collett, Gordon, B.Sc., 49 Liverpool-road, Summer Hill.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1913	P 5	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1940		Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
1919		Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
1909	P 7	Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
1940		Cox, Morris Edward.
1941	P 1	Craig, David Parker, Research Scholar, 62 Springdale-road, Killara.
1921	P 1	‡Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street, Rockdale.
1940	P 4	Crockford, Joan Marian, B.Sc., 219 Victoria-road, Gladesville.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
1906		‡Dixson, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.I.C., F.A.C.I., 30 Hampden-road, Pennant Hills.

Elected.		
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney ; p.r. 18 Hillview-street, Sans Souci.
1937	P 7	Dulhunty, John Allan, B.Sc., Geology Department, University of Sydney.
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney ; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1934	P 19	Dwyer, Francis P. J., M.Sc., Lecturer in Chemistry, Technical College, Sydney.
1923	P 21	Earl, John Campbell, D.Sc., Ph.D., Professor of Organic Chemistry in the University of Sydney. (President, 1938.)
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.I.C., Professor in Engineering Technology and Metallurgy in the University of Sydney.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
1940		Emmerton, Henry James, B.Sc., 41 Nelson-street, Gordon.
1937		English, James Roland, L.S. A.I.F.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland ; p.r. Regent-street, West Maitland.
1908		‡Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. *Lond.*, A.R.A.I.A., 6 Major-street, Coogee.
1921		Farnsworth, Henry Gordon, Government Stores, Harrington-street, Sydney ; p.r. "Rothsay," 90 Alt-street, Ashfield.
1939		Faull, Norman Augustus, M.Sc., c/o National Standards Laboratory, University Grounds, City-road, Chippendale.
1909	P 7	Fawsitt, Charles Edward, D.Sc., Ph.D., Professor of Chemistry in the University of Sydney. (President, 1919.)
1923		Fiaschi, Piero, O.B.E., V.D., M.D. *Columbia Univ.*, D.D.S. *New York*, M.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 178 Phillip-street, Sydney.
1940		Finch, Franklin Charles, B.Sc., 1 Linden Court, Windsor, S.1, Melbourne.
1927	P 7	Finnemore, Horace, B.Sc., F.I.C., Reader in Pharmacy in the University of Sydney.
1940		Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
1920		Fisk, Sir Ernest Thomas, K.B., F.Inst.R.E., A.M.I.E. *Aust.*, Chairman of Directors, Amalgamated Wireless (Australasia) Ltd., Wireless House, 47 York-street, Sydney ; p.r. 16 Beaconsfield-parade, Lindfield.
1940		Flack, Arthur Charles Allenby, B.Sc., Agricultural High School, Yanco, N.S.W.
1933		Fletcher, Harold Oswald, Assistant Palæontologist, Australian Museum, College-street, Sydney.
1879		‡Foreman, Joseph, M.R.C.S. *Eng.*, L.R.C.P. *Edin.*, "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c/o Department of Aircraft Production, Box 20935, Melbourne, Vic.
1905		‡Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1940		Freney, Martin Raphael, B.Sc., McMaster Laboratory, Sydney.
1935	P 2	Garretty, Michael Duhan, M.Sc., Chief Geologist, North Broken Hill Ltd., Broken Hill, N.S.W.
1939	P 2	Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney ; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
1942		Gibson, Neville Allan, B.Sc., Industrial Chemist, 217 Parramatta-road, Haberfield.
1940		Gillis, Richard Galvin, 1 Dundee, 35 Adams-street, South Yarra, S.E.1, Vic.
1935		Goddard, Roy Hamilton, F.C.A. *Aust.*, Royal Exchange, Bridge-street, Sydney.
1936		Goulston, Edna Maude, B.Sc., p.r. 83 Birriga-road, Bellevue Hill.
1940		Graves, John Nevil, B.Sc., 96 Wentworth-street, Randwick.
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.I.C., Chief Chemist, Department of Agriculture ; p.r. 151 Wollongong-road, Arncliffe.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney ; p.r. 15A Wharf-road, Longueville.
1892		‡Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney ; p.r. 23 March-street, Bellevue Hill.

Elected.		
1940		Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney; p.r. 4 Pearson-avenue, Gordon.
1905	P 6	‡Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield.
1936		Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
1937	P 8	Harradence, Rita Harriet, D.Phil. (*Oxon.*), M.Sc. (*Syd.*), Research Scholar, c/o Dyson Perrins Laboratory, Oxford University, Oxford, England.
1934		Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1923	P 3	Harrison, Travis Henry John, D.Sc.Agr., D.I.C. *London*, Commonwealth Fruit Officer, Australia House, Strand, London, England; p.r. 41 Queen's Gardens, Ealing, W.5, London.
1929		Hawley, J. William, J.P., Financial Agent, 4 Castlereagh-street, Sydney; p.r. 12 King's-road, Vaucluse.
1934		Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c/o Messrs. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 101 Essex-street, Epping.
1919		Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1940		Heselton, Thomas William, B.Sc., c/o Munition Laboratories, Maribyrnong, Victoria.
1938	P 4	Hill, Dorothy, M.Sc. *Q'ld.*, Ph.D. *Cantab.*, Geological Research Fellow, University of Queensland, Brisbane.
1918		Hindmarsh, Percival, M.A., B.Sc.Agr., Principal, Hurlstone Agricultural High School, Glenfield.
1936		Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
1928		Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (*Aust.*), A.M.Inst.T.; p.r. "St. Cloud," Beaconsfield-road, Chatswood.
1916		Hoggan, Henry James, A.M.I.M.E. *Lond.*, A.M.I.E. *Aust.*, Consulting and Designing Engineer, "Lincluden," 81 Frederick-street, Rockdale.
1941		Howard, Harold Theodore Clyde, B.Sc., Principal, Wollongong Technical High School, Wollongong.
1935		Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
1936		Howie, Sir Archibald, K.B., M.L.C., 7 Wynyard-street, Sydney.
1938	P 4	Hughes, Gordon Kingsley, B.Sc., Lecturer in Chemistry, University of Sydney.
1923	P 3	‡Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
1942	P 1	Jaeger, John Conrad, M.A., D.Sc., c/o Radiophysics Laboratory, The University, Sydney.
1940		Johns, Thomas Harley, 130 Smith-street, Summer Hill.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1935	P 6	Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1911		Julius, Sir George A., Kt., B.Sc., B.E., M.I.Mech.E., M.I.E.Aust., Culwulla Chambers, Castlereagh-street, Sydney.
1935		Kelly, Caroline Tennant (Mrs.), "Eight Bells," Castle Hill.
1935		Kelly, Francis Angelo Timothy, "Eight Bells," Castle Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, c/o Australian Paper Mfrs. Ltd., Macauley-street, Matraville; p.r. 55 Harold-street, Matraville.
1940		King, Leonard Esmond, 161 Nelson Bay-road, Bronte.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.
1939		Lambeth, Arthur James, B.Sc., 44 Meek-street, Kingsford.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., P.O. Box. No. 21, Concord.
1924		Leech, Professor Thomas David James, B.Sc., B.E. *Syd.*, Professor of Engineering, Auckland University College, Auckland, N.Z.

Elected.		
1934		Leech, William Dale, Californian Institute of Technology, Pasadena, California, U.S.A.
1936	P 3	Lemberg, Max Rudolf, D.Phil., Biochemist, Royal North Shore Hospital; p.r. 12 de Villiers-avenue, Chatswood.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1940		Lincoln, Gordon James, B.Sc., 15 Turner-avenue, Haberfield.
1929	P 55	‡Lions, Francis, B.Sc., Ph.D., A.I.C., Department of Chemistry, University of Sydney; p.r. 31 Chesterfield-road, Epping.
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1940	P 1	Lipson, Menzie, B.Sc., Chemist, C.S.I.R., Central Wool Committee Testing House, 17 Randle-street, Sydney; p.r. 5 Phillip Court, Latimer-road, Rose Bay.
1940	P 1	Lockwood, William Hutton, B.Sc., Institute of Anatomy, Canberra, A.C.T.
1906		‡Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1927	P 1	Love, William Henry, B.Sc., Ph.D., Lecturer in Physics, University of Sydney.
1940		Luciano, Albert Anthony, 16 Arthur-street, Bellevue Hill.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 8 Boronia-avenue, Wollstonecraft.
1939	P 1	Maccoll, Allan, M.Sc., 76 Springdale-road, Killara.
1940		Maccoll, Mrs. Margaret Elphinstone, B.A., B.Ec., 76 Springdale-road, Killara.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2	‡McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	‡McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1932		McKie, Rev. Ernest Norman, B.A. *Syd.*, St. Columba's Manse, Guyra.
1927		McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W.
1940		Malone, Edward E., No. 4, Astral, 10 Albert-street, Randwick.
1924		Mance, Frederick Stapleton, "Binbah," Lucretia-avenue, Longueville.
1935		Maze, Wilson Harold, M.Sc., Lecturer in Geography, University of Sydney.
1941		Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1912		Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
1929	P 18	Mellor, David Paver, M.Sc., Lecturer, Chemistry Department, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42.)
1940		Mercer, Edgar Howard, McMaster Laboratory, Parramatta-road, Glebe.
1928		Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood.
1940		Mills, James Edward, M.Sc., Ph.D., 16 Smith-road, Artarmon.
1940	P 1	Morris, Benjamin Sydney, B.Sc., 22 Kelso-street, Enfield.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P 27	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney.
1934		Mort, Francis George Arnot, Manufacturing Chemist, 16 Grafton-street, Woollahra.
1915		Murphy, Robert Kenneth, Dr.Ing., Chem.Eng., A.S.T.C., M.I.Chem.E., A.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.
1940		Murray, Alban James Moore, B.Sc., 54 Sydney-road, Willoughby.
1923	P 2	Murray, Jack Keith, QX34748, B.A., B.Sc.Agr., N.E. Reinf. Training Centre, Warwick, Queensland, and Professor of Agriculture in the University of Queensland.
1930	P 6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.F., Squadron Leader, R.A.A.F., Headquarters, Melbourne; p.r. "Kingsleigh," Ingleburn, N.S.W.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Biology, Victoria University College, Wellington, N.Z.
1935		Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
1938	P 1	Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., Secretary, Linnean Society of N.S.W., Science House, Gloucester-street, Sydney.

Elected.		
1920	P 4	‡Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)
1940		Norrie, Jack Campbell, B.Sc., 28 Ray-road, Epping.
1940	P 6	Nyholm, Ronald Sydney, M.Sc., 77 Bland-street, Ashfield.
1935		O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
1903		‡Old, Richard, "Waverton," Bay-road, North Sydney.
1921	P 5	Osborne, George Davenport, D.Sc. *Syd.*, Ph.D. *Camb.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1920	P 74	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo; p.r. 67 Park-avenue, Roseville. (President, 1935.)
1933		Penman, Arthur Percy, B.E. *Syd.*, Mining Engineer, 10 Water-street, Wahroonga.
1940		Pettingell, William Walter, B.Sc., 28 Conder-street, Burwood.
1938		Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliffe.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
1896		‡Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
1921	P 2	Powell, Charles Wilfrid Roberts, F.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1918		Powell, John, Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
1918		Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
1893		‡Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	‡Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
1922	P 5	Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
1940		Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
1936		Randall, Harry, Buena Vista-avenue, Denistone.
1931	P 1	Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Mineral Resources Survey, Department of Supply and Shipping, Census Building, Canberra, A.C.T.
1935		Reid, Cicero Augustus, 19 Newton-road, Strathfield.
1932		Richardson, Henry Elmar, Chemist, Chase-road, Turramurra.
1939	P 6	Ritchie, Ernest, B.Sc., 6 Military-road, North Bondi.
1933		Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
1940		Robertson, Rutherford Ness, B.Sc. *Syd.*, Ph.D. *Cantab.*, Flat 4, 43 Johnston-street, Annandale.
1935		Robinson, Albert Jordan, Managing Director, S. T. Leigh & Co. Ltd., Raleigh Park, Kensington.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.

Elected.		
1928		Ross, Allan Clunies, B.Sc., F.C.A. *Aust.*, Chartered Accountant *Aust.*, 54A Pitt-street, Sydney; p.r. The Grove, Woollahra. (Member from 1915 to 1924.)
1940		Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
1929		Royle, Norman Dawson, M.D., Ch.M., 185 Macquarie-street, Sydney.
1940		Sarroff, Carlyle Joseph.
1935		Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
1941	P 1	Sawkins, Dansie Thomas, M.A. *Syd.*, B.A. *Camb.*, Reader in Statistics, The University, Sydney; p.r. 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.Sc. *Syd.*, A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1940		Scott, Reginald Henry, B.Sc., 154 Highfield-road, Camberwell, Vic.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, Marist Brothers' College, Randwick, N.S.W.
1938		Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, 2 Edward-street, Gordon.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. *Melb.*, 43 Robertson-road, Centennial Park.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1900		‡Simpson, R. C., Lecturer in Electrical Engineering, Technical College, Sydney.
1933		Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Ltd., Manufacturing Chemists, 23 Rosebery-avenue, Rosebery; p.r. "Raiatea," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, 1 Rocklands-road, Wollstonecraft.
1922	P 1	Smith, Thomas Hodge, Australian Museum, College-street, Sydney.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboonoo," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1900	P 1	‡Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney.
1909		Stokes, Edward Sutherland, M.B., Ch.M. *Syd.*, D.P.H. *Irel.*, Medical Officer, Metropolitan Board of Water Supply and Sewerage, 341 Pitt-street, Sydney; p.r. 15 Highfield-road, Lindfield.
1916	P 1	Stone, Walter George, F.S.T.C., A.A.C.I., Senior Analyst, Department of Mines, Sydney; p.r. 14 Rivers-street, Bellevue Hill.
1940		Stroud, Richard Harris, B.Sc., "Dalveen," corner Chalmers and Barker-roads, Strathfield.
1918		‡Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1901	P 16	‡Sussmilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (President, 1922.)
1919		‡Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*, Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1941		Suvoroff, Victoria, B.Sc., Chief Chemist and Metallurgist, c/o G. E. Crane & Sons, Pty., Burwood-road, Concord.
1941	P 2	Swanson, Thomas Baikie, M.Sc. *Adel.*, Lecturer in Chemistry, New England University College, Armidale.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1939		Thomas, Mrs. A. V. M., 12 Clifton-avenue, Burwood.
1919		Thorne, Harold Henry, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.

Elected.		
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., P.O. Box 97, Atherton, North Queensland.
1923		Toppin, Richmond Douglas, A.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
1932	P 8	Trikojus, Victor Martin, B.Sc., D.Phil., Professor of Biochemistry, The University, Melbourne.
1940		Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co., 1 O'Connell-street, Sydney.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, M.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 9	‡Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney. (President, 1930.)
1919	P 1	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913.)
1913	P 5	Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
1921		‡Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., 39 Stanhope-road, Killara.
1924		Waterhouse, Leslie Vickery, B.E. *Syd.*, Mining Engineer, Shell House, Carrington-street, Box 58 CC, G.P.O., Sydney; p.r. 4 Bertha-road, Neutral Bay.
1919	P 1	Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 5	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Reader in Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
1941	P 1	Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of Agriculture, University of Sydney.
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1936		Wearne, Harold Wallis, 22 Yarabah-avenue, Gordon.
1920	P 1	Wellish, Edward Montague, M.A., Associate-Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1940	P 1	White, Douglas Elwood, M.Sc., D.Phil., Chemistry Department, The University, Melbourne.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, 143 Macquarie-street, Sydney; p.r. Jersey-road, Strathfield.
1942		Williams, Gordon Roy, B.Sc., 45 Conder-street, Burwood.
1940		Willison, Alan Maynard, M.Sc., 3 Stanley-street, Randwick.
1940		Wogan, Samuel James, 34 Neich-parade, Burwood.
1936	P 1	Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Assistant Astronomer, Sydney Observatory; p.r. 4 Ormond-street, Ashfield.
1906	P 12	‡Woolnough, Walter George, D.Sc., F.G.S., No. 4, "Aylesbury," 152A Ernest-street, North Sydney. (President, 1926.)
1916		Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 16 Barrack-street, Sydney; p.r. "Wanawong," Castle Hill, N.S.W.
1921		Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turramurra.

Honorary Members.

Limited to Twenty.

Elected.	
1939	Chapman, Frederick, A.L.S., F.R.S.N.Z., F.G.S., "Hellas," 50 Stawell-street, Kew, E.4, Victoria.
1914	Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1931	Lyle, Sir Thomas Ranken, K.B., C.B.E., M.A., D.Sc., F.R.S., "Lisbuoy," Irving-road, Toorak, Melbourne, Victoria.
1915	Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912	Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.
1922	Wilson, James T., M.B., Ch.M. *Edin.*, F.R.S., Professor of Anatomy in the University of Cambridge; p.r. 24 Millington-road, Cambridge, England.

Obituary, 1942-1943.

Elected.	
1894	James Adam Dick.
1913	John Clifford Firth.
1880	Gerald Harnett Halligan.
1896	Kelso King.
1913	Archibald Durrant Ollé.
1920	Marcus Baldwin Welch.
1915	Joseph J. Thompson (Honorary Member).

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke " as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories ; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. " The Volcanoes of Victoria," and " The Origin of Dolomite " (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.

1907. " Geography of Australia in the Permo-Carboniferous Period " (two lectures). By Professor T. W. E. David, B.A., F.R.S.
" The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
" Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
" The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.

1918. " Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.

1919. " Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.

1936. " The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (This Journ., 1936, *70*, 39.)

1937. " Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (This Journ., 1937, *71*, 68.)

1938. " The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (This Journ., 1938, *71*, 503.)

1939. " Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (This Journ., 1939, *73*, 41.)

1940. " The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (This Journ., 1940, *74*, 283.)

1941. " The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (This Journ., 1941, *75*, 47.)

1942. " The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of
The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 *to* 1878.

The prefix * indicates the decease of the recipient.

Awarded.

1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
1879 *George Bentham, C.M.G., F.R.S.
1880 *Professor Thos. Huxley, F.R.S.
1881 *Professor F. M'Coy, F.R.S., F.G.S.
1882 *Professor James Dwight Dana, LL.D.
1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
1886 *Professor L. G. De Koninck, M.D.
1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.

Awarded.

1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
1893 *Professor Ralph Tate, F.L.S., F.G.S.
1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, C.M.G., F.L.S.
1903 *Alfred William Howitt, D.Sc., F.G.S.
1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
1909 *Dr. Walter E. Roth, B.A.
1912 *W. H. Twelvetrees, F.G.S.
1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, F.G.S.
1921 *Joseph James Fletcher, M.A., B.Sc.
1922 *Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925 *Charles Hedley, F.L.S.
1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
1932 Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.
1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
1938 Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
1939 C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

Awarded.

1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Freshwater Invertebrate Fauna of Port Jackson and Neighbourhood."

Awarded.

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. Burfitt, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (This Journal, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
1940 G. J. Burrows, B.Sc., University of Sydney.
1942 J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.

ISSUED OCTOBER 15, 1942

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JOURNAL AND PROCEEDINGS

OF THE

ROYAL SOCIETY

OF NEW SOUTH WALES

FOR

1942

(INCORPORATED 1881)

PART I (pp. 1 to 95)

OF

VOL. LXXVI

Containing Papers read in April and May

EDITED BY

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1942

CONTENTS

VOLUME LXXVI

Part I

Page.

ART. I.—Presidential Address. By D. P. Mellor, M.Sc. (Issued September 21, 1942) 1

ART. II.—Methæmoglobin Formation. By John Williamson Legge, B.Sc. (Issued September 21, 1942) 47

ART. III.—A Note on the Essential Oil of *Eucalyptus conglobata* var. *aneeps*. By P. A. Berry, M.Sc., and T. B. Swanson, M.Sc. (Issued August 12, 1942) 53

ART. IV.—Studies in Metamorphism and Assimilation in the Wellington District, N.S.W. II. The Dynamic and Contact Metamorphism of a Group of Ultrabasic Rocks. By Elizabeth M. Basnett, M.Sc. (Issued September 21, 1942) 55

ART. V.—The Tertiary Land Surface in Southern New England. By A. H. Voisey, M.Sc. (Issued September 21, 1942) 82

ART. VI.—Spermatorrhœa in Marsupials, with Special Reference to the Action of Sex Hormones on Spermatogenesis of *Trichosurus vulpecula*. By Adolph Bolliger, Ph.D. (Issued September 21, 1942) 86

ART. VII.—The Occurrence of Two Physiological Forms of *Leptospermum citratum* (Challinor, Cheel and Penfold) as Determined by Chemical Analysis of the Essential Oils. By A. R. Penfold, F.A.C.I., F.C.S., F. R. Morrison, A.A.C.I., F.C.S., and S. Smith-White, B.Sc.Agr. (Issued September 21, 1942) 93

PRESIDENTIAL ADDRESS

By D. P. MELLOR, M.Sc.

Delivered to the Royal Society of New South Wales, April 1, 1942.

PART I. THE PAST YEAR.

As the present world conflict grows more widespread, it is inevitable that there will be an increasing diversion of science from its normal peace-time activities and a consequent diminution in the output of fundamental research work. We must accept this as a condition of the survival of science as we know it, and it is in this light that we must view the falling off in the number of papers received for reading and publication from 40 in 1940 to 20 in 1941. A part of the fall may be due to a normal fluctuation, the remainder reflects the prevailing conditions. The number of our exchanges is also falling steadily, having dropped from 268 to 239 during the past year and from 361 since May, 1939. We will be fortunate indeed if our difficulties in the coming months are no more than these.

In thus commencing the survey of the past year I have drawn the worst side of the picture first. Actually most activities of the Society have followed their usual courses. The membership stands at the satisfactory total of 298, gains during the year roughly counterbalancing losses. Several years ago (1935) women were admitted to the Society for the first time. As a logical sequence to this I am pleased to be able to report the first election of a woman member, Dr. Ida Brown, to the Council. To another of our Council members, Professor T. G. Room, has fallen the signal distinction of election to the F.R.S., and we offer him our heartiest congratulations.

In addition to the twenty papers accepted for reading and publication during the year, the following short addresses were given :

" Fiji and the Fijians ", by Arthur Capell, M.A., Ph.D.

" Mineral Resources of the Great Powers in Relation to the International Situation ", by G. D. Osborne, D.Sc.

" A Scale of Magnitudes ", by F. Lions, Ph.D.

" The Electron Microscope ", by R. E. B. Makinson, Ph.D.

" Vitamin B_1—its Discovery and Importance in Nutrition and Disease-prevention ", by A. Bolliger, Ph.D.

" The Sulphanilamide Drugs ", by F. Lions, Ph.D.

The following exhibits were shown at meetings :

" Some Recent Developments in Plastics ", by F. R. Morrison, A.A.C.I.

" A Fluorescent Chromatographic Column ", by A. J. Tow, B.Sc.

" The Jelley-Leitz Refractometer ", by G. D. Osborne, D.Sc.

By courtesy of the Rural Bank of N.S.W., films were shown and a commentary provided, on " The Menace of Soil Erosion " and " The Red Terror " (bush fires).

Popular lectures dealing with a wide variety of topics were delivered during the months of June to October (inclusive) and were well attended. They were :

19th June.—" Some Aspects of Hydatid Disease in Australia ", by Professor H. Dew, M.B., B.S., F.R.C.S.

17th July.—" The Modern Aeroplane ", by Professor A. V. Stephens, M.A.

21st August.—" War and the Fisheries ", by H. Thompson, M.A., D.Sc.
18th September.—" Weighing the Stars ", by R. van der R. Woolley, M.Sc., Ph.D.
16th October.—" The Cow, the Chemist and Ourselves—The Nutrition of Farm Animals in Plenty and in Drought ", by E. G. Hallsworth, B.Sc., Ph.D.

The Society is indebted to the lecturers who kindly gave their services on the above occasions. Owing to uncertainty about conditions which may prevail in the coming winter months, the Council has decided to abandon the ordinary form of popular lecture, for the time being at least, and to use the present as an opportunity for trying out a new experiment. Arrangements are in hand for a series of popular broadcast talks to be delivered over the national stations, under the Society's auspices. In the absence of facilities for experiment and illustration there is no doubt that broadcasting will prove a more difficult medium for a popular lecture, if it is to deal with more than the magic and gadgetry of science. It may be that the limitations of the medium and of the time available for each talk do not permit one to go any deeper than this. Experience alone will prove whether or not it will be wise to incorporate broadcast talks by experts in their particular fields as a permanent part of our popular science programme.

One symposium was held during the year, the subject chosen for discussion being " Light Metals ". The following were the speakers and subjects :

" Sources of Light Metals ", Professor L. A. Cotton.
" Manufacture of and Demand for Light Metals ", Dr. J. E. Mills.
" Some Alloys of the Light Metals ", Miss V. Suvoroff, B.Sc.

Like the symposia held in previous years, this one proved most valuable and interesting. So far, practically all our symposia have been devoted to the various elements, sulphur, phosphorus, potassium, etc. It would seem worth while now to strike out into new fields, even if it is difficult to find a subject which provides a suitable common meeting ground for different specialists.

The tenth Clarke Memorial Lecture was delivered on 22nd May, 1941, by Mr. C. A. Sussmilch, and was entitled " The Climate of Australia in Past Ages ". The Clarke Memorial Medal for 1941 was awarded to Professor Wood Jones, F.R.S., formerly of the Universities of Adelaide and Melbourne, and later Professor of Anatomy in the University of Manchester. The medal was presented to Professor Wood Jones at the Anniversary Meeting of the Royal Society (London), held on 1st December, 1941.

The Walter Burfitt Prize was awarded to Frederick W. Whitehouse, D.Sc., Ph.D., Lecturer in Geology in the University of Queensland.

It is perhaps a little disappointing to have to report that the revision of Rules was not completed before the end of the year. What started as the revision of a few Rules finished up as the revision of Rules from beginning to end. The magnitude of the task and wisdom of hastening slowly were largely responsible for the prolongation of this work.

I should here like to place on record my appreciation of the untiring efforts of all those who served on this and other committees throughout the year. On my own and your behalf I sincerely thank members of the Council for their help and loyal cooperation. I would especially mention the two Honorary Secretaries, Professor A. P. Elkin and Dr. C. Anderson, upon whom so many of the burdens of the Society fall. Our thanks are also due to the chairmen and honorary secretaries of Sections ; to the Librarian, Mr. W. H. Maze, and his assistant, Dr. A. Bolliger, who with the help of Dr. Anderson did yeoman service in restoring order to the Society's vast collection of old volumes of the Journal.

The Journal.

It is widely recognised that one of the most important functions of our Society is the publication of the Journal, and in this connection I have to record several events of interest. Perhaps the most noteworthy is the enlargement of the format. I should explain that this was done not to improve the appearance of the Journal—from an æsthetic point of view the old size probably had more to recommend it—but for reasons of economy and efficiency. A very thorough analysis of the costs of publishing scientific periodicals has been carried out under the auspices of the National Research Council (U.S.A.).[1] From this it was clear that economies could be effected in the publication of our Journal. It was shown, for example, that as the number of words per page increases, so the cost per word per 1,000 copies of a journal (the basis for comparison) diminishes. An upper limit is set to the number of words per page and page size, by considerations of handling and shelving bound volumes, and there is no danger that any enthusiast will so extend the enlarging process as one day to startle members with a volume of newspaper size. For a time the Journal may appear painfully slim, but I hope that, as better times return, it will assume its usual substantial appearance.

During the year a small pamphlet entitled " Guide to Authors " was compiled by a committee and published for the mutual assistance of editors and authors. It is hoped that it will prove helpful in regard to such matters as standard nomenclature, symbols and abbreviations for titles of journals, etc.[2]

The maintenance of the quality of papers for a journal is, to some extent, dependent on refereeing. Several changes, designed to assist referees in their task, have recently been introduced. Among these is the issue of a special printed form which sets out clearly the course of action open to a referee and, when signed, serves as a kind of standardised certificate in regard to the character of the paper with which it is duly filed.

Scientific Periodicals.

During the year several questions relating to periodicals have come up for discussion both by the Council and Library Committee. Among the results of these discussions was the passing of a resolution by the Council to the effect that our library be essentially one for scientific periodicals. The question of a central library for Science House was again canvassed, but I regret to say that there is no immediate prospect of any move in this direction. However, the enquiry was not altogether barren of results, as it stimulated further investigation into the overlapping between our own library and that of the Linnean Society. The overlapping here is considerable but there is every prospect of a reduction where duplication is proved unnecessary. It is recognised that some duplication may be desirable and that each case must be considered on its merits.

I should like to see steps to eliminate unnecessary duplication and to effect closer coordination taken further and extended to cover all the important periodical libraries in Sydney. An example, chosen at random, will serve to show the kind of thing that may happen in the absence of some coordination. The Royal Society purchases a journal known as the " Observatory ", for which there is, I understand, little demand by our members. The same journal is taken by the Government Observatory and the Public Library, both copies being readily available to *bona fide* enquirers. Other instances of this kind of duplication could be found, and it is clear that the Society would be assisting the cause of science here by dropping unnecessary duplication so that it might fill some important gaps in the supply of scientific periodicals. I believe that

[1] J. R. Schramm, 1939. *Proc. Amer. Phil. Soc.*, **80**, 1.

[2] See also " Abbreviations for Titles of Scientific Periodicals ", 1941, *Aus. J. Sci.*, **4**, 71.

by steps of this kind we might greatly improve the usefulness of, and demand for, the facilities of our library. Many of us are aware of important journals that are not available in Australia and equally well aware that funds are not likely to be forthcoming for their purchase in the near future. By proper coordination and without putting undue strain upon the present satisfactory inter-library borrowing system, I feel sure that the situation could be improved with little or no further financial expenditure. I may be a little over-optimistic about the prospects in this direction, but at least the experiment would be worth trying. The Society might well take the initiative in forming a representative committee of members of scientific societies and professional librarians to look into the whole question of coordination of scientific periodical collections in Sydney.

A Central Register of Scientific and Trained Personnel.

If we are to make wise and efficient use of our national resources, an indispensable prerequisite would seem to be that we at least know what they are and where they are. Yet, in regard to one important field of our human resources, namely that covering scientific and trained personnel, we, in this country, have done next to nothing to answer either of these questions. In this we lag far behind England and U.S.A., where it is widely recognised that a complete central register of scientific personnel is a *sine qua non* for the efficient use of brain power in time of national emergency. At the present moment the Commonwealth Government is engaged in making a national register of all its citizens between 16 and 60, but in regard to scientists it does not go nearly far enough. The scope of the information required can be seen from a glance at the American questionnaires.[3] It is too late for any survey to be of use in the crises expected in the coming months, but in the long distance struggle ahead there can be no doubt of its usefulness. Experience in England and U.S.A. has already proved the registers of great national value, and there is every evidence that this will be true in times of peace no less than war. It is the latter that concerns us most closely now. "A chemist whose work has been done in some specialised and relatively obscure field may suddenly become the one man in the country able to devise a means of protection against some new chemical weapon. A specialist in an obscure dialect of a foreign language may possess a skill which will have a far-reaching significance in an emergency." Our chances of locating such individuals with speed and certainty when required are considerably greater if a properly devised national register is available.

A country without a register may be likened to a library whose books are neither systematically arranged nor catalogued, and just as a catalogue does not in itself guarantee that a library will be well used, so it is with a national register of scientific and trained personnel. There is no sense in making a national register if it is not going to be widely and wisely used by the civil services, the fighting services and private institutions of all kinds.

It is true that some sectional registers of chemists, engineers, etc., have already been compiled, but there is evidence that the registers have not been as widely used as they might and also evidence of a general lack of centralisation. The English register was compiled under the auspices of the Royal Society of London. The job is much too big for the limited resources of such a society as our own, or even of the Australian National Research Council, which is attempting to do something about the matter. The administration of such a scheme would seem more properly to belong to the sphere of the Federal Government as it is in U.S.A. The most this Society can do is to lend the

[3] For information on the national roster of scientific personnel in U.S.A., see Carmichael, L., 1940, *Science*, **92**, 135; 1941, **93**, 217; 1942, **95**, 86.

weight of its authority to advocating such a scheme, and in the event of it coming into being to proffer the advice of its specialists in regard to the details of the register.

The Award of Medals.

Last year your President (Professor A. P. Elkin) suggested the revival of the practice of awarding the Society's medal together with substantial prize money for meritorious work without limitation of the field of research. While nothing has yet been done to implement this suggestion, it has not been lost sight of. Experience of the past year confirms that of previous years that there is need for the revival of the practice of awarding the Society's own medal to supplement the awards which are now made on the basis of certain benefactions. This presupposes, of course, that there is general agreement on the practice of making awards of medals at all. To satisfy my own doubts on this matter I turned to the records relating to the awards of medals by the Royal Society of London, and there I came across what to my mind is an excellent statement of the arguments for and against honorary rewards. In concluding this part of my address, I will take the liberty of quoting it to you at some length, in the hope that when the question comes up for consideration it may prove useful as a basis for discussion.

> "It is said that they must either confirm or contradict the judgment which has been either already pronounced, or which Posterity will most certainly hereafter pronounce, upon the merits, pretensions and influence of the discoveries or series of investigations which such medals are designed to commemorate; that in the first case they can confer no additional honour upon their author, whose rank has already been ascertained and fixed by the sentence of a higher tribunal, while, in the second, they can only tend to compromise the character of the scientific body by whose advice they are conferred. It is true that I would not claim infallibility for the united judgment of any association, or body of men, however eminent their scientific rank may be: but it is the peculiar privilege of the great masters of science (and more particularly so when acting or speaking as a body), to be able to anticipate, though not without the possibility of error, the decision of Posterity, and thus to offer to the ardent cultivator of science that highest reward of his labours, as an immediate and well assured possession, which he might otherwise be allowed silently and doubtingly to hope for, but never be permitted to see realised; and though some powerful minds might be content to trust the complete development of their fame to the fullness of time, and might pursue their silent labours under the influence of no other motives but such as are furnished by their love of truth, the gratification derived from the discovery of the beautiful relations of abstract science, or from the contemplation of the agency of a Divine Mind in the harmonies and constitution of the physical world, yet it is our duty and business to deal with men as we find them constituted, and to stimulate their exertions by presenting to their view honourable distinctions attainable by honourable means; to assure them that the results of their labours will neither pass unnoticed nor unrewarded; and that there exists a tribunal to which they may appeal, or before which they can appear, whose decision is always for honour, never for condemnation . . ."—H.R.H. Duke of Sussex, K.G., F.R.S., *J.P. of R.S.*, vol. XLVII, 106.

Obituary.

I regret to record the deaths during the past year of the following members: Richard Thomas Baker, Edward George Noble and Carl Gustav Sundström.

Richard Thomas Baker died at his residence, Cheltenham, N.S.W., on the 14th July, 1941, at the age of 87. Mr. Baker was born at Woolwich, Kent, England, on the 1st December, 1854. He came to Australia in September, 1879. In June, 1880, he joined the staff at Newington College, Sydney, as Senior Housemaster and Science and Art Master, a position he subsequently resigned upon his appointment in June, 1888, to the scientific staff of the Sydney Technological Museum. Mr. Baker became Curator and Economic Botanist in 1901 in succession to J. H. Maiden, and continued in that position until his retirement in 1920.

Mr. Baker became a member of this Society in 1894 and contributed twenty-eight papers to the Journal and Proceedings. Altogether he published over 100 original papers in the Journal and Proceedings of this Society as well as in the Journal and Proceedings of the Linnean Society of New South Wales. Mr. Baker's name will always be remembered for his collaboration with the late H. G. Smith in a celebrated series of investigations into the economics of the eucalypts. The results were published in 1902 in a volume entitled " A Research on the Eucalypts and Their Essential Oils ". This was revised and republished as a second edition in 1920 upon the retirement of the authors from the Public Service of New South Wales.

The outstanding feature of their work was a classification of the eucalypts based on the chemical characters of the essential oils derived from each species. The use of this method as an aid to the morphological classification has given valuable results and contributed greatly to our knowledge of the Australian flora.

In addition, Mr. Baker was the author of a number of monographs on other groups of Australian forest plants and their economic products. He was joint author with Mr. H. G. Smith in a publication issued in 1910 entitled " A Research on the Pines of Australia ", which was a further example of the successful collaboration between botanist and chemist. A number of other useful technical books were published by Mr. Baker during his career: " Building and Ornamental Stones of Australia ", " Cabinet Timbers of Australia ", " The Australian Flora in Applied Art " and " Hardwoods of Australia ", which latter he claimed as his *magnum opus*. He was the protagonist for the adoption of the waratah as our national emblem in place of the wattle.

Mr. Baker occupied the position of Lecturer in Forestry to the University of Sydney from 1913 to 1924. He was a Fellow of the Linnean Society of London and served on the Council of the New South Wales Society during the period 1897 to 1922.

Mr. Baker was the recipient of several honours from scientific societies for his researches in pure and applied science. In 1921 he was awarded the Mueller Medal by the Australian Association for the Advancement of Science, and in 1922 he received the Clarke Memorial Medal of the Royal Society of New South Wales. He was an honorary member of the Pharmaceutical Societies of Great Britain and New South Wales and the College of Pharmacy, Philadelphia, United States of America.

Edward George Noble, who died on 4th May, 1941, aged 76, was a life member of the Royal Society, which he had joined in 1891. He was a licensed surveyor and civil engineer. After some years in the Public Works Department, he was appointed as Assistant Engineer to Mr. Milner at Newcastle to carry out the sewerage works.

At the outbreak of the last war of 1914-18, while travelling to Rabaul, the *Matunga*, on which he was a passenger, was seized by the raider *Wolf*, and Mr. Noble became a prisoner in Germany for the duration of the war. In later years he was employed at St. Andrew's Cathedral on survey work.

Mr. Noble, who was the brother of the Rev. H. J. Noble and of M. A. Noble, the noted cricketer, left a widow and four daughters.

Carl Gustaf Sundström was elected to the Society in 1918. He was born at Norrköping, Sweden, in 1882, and died on the 5th July, 1941. He left Sweden at an early age and after several trips around the world settled in Australia where later, in 1913, he founded the Federal Match Co. at Alexandria, Sydney. From very small beginnings the factory now occupies five acres and is looked upon as a model industrial establishment in many respects.

Mr. Sundström took a very active interest in the technical branch of the factory, and was a keen student of chemistry, being for many years a member of the Sydney Technical College Chemical Society. He was very energetic in the discharge of his duties and was noted for his administrative ability.

His activities outside of the scientific world were numerous, and his boundless generosity made him extremely popular in these spheres.

Part II. THE STEREOCHEMISTRY OF SQUARE COMPLEXES.

In the design of molecules Nature uses relatively few fundamental units of pattern or configurations, and it is naturally important to know what these are and under what circumstances any particular configuration is likely to be found. We shall here be concerned with the narrow field of stereochemistry which deals with the orientation in space of the four valence bonds of quadricovalent elements. The tetrahedral disposition of four valence bonds about the carbon atom was the first configuration to be discovered, and so widespread did its occurrence eventually prove to be, not only among the compounds of carbon, where it was universal, but also among some forty other elements, that attention to this type of structure for long overshadowed that given to an alternative arrangement of four bonds in space, namely the square arrangement. Indeed, the tetrahedral arrangement proved to be so dominant a feature of molecular architecture that the very existence of the square pattern was, and for that matter, in some quarters, still is, a matter of controversy. Nevertheless the evidence on this question has grown steadily over the last few years and the time is opportune for some attempt to evaluate the significance of the square configuration for the stereochemistry of the metals.

In attempting to do this, two main questions will be considered: firstly, how strong is the evidence for the square disposition of valence bonds, and secondly, with what elements and under what circumstances does it occur? In tracing the developments leading to the proof of square coordination, attention will be centred on the compounds of platinous platinum (Pt^{II}), because it is with these that the most abundant and satisfactory evidence has been obtained. Notwithstanding this, there has been a good deal of controversy about the structure of platinum compounds. Some idea of the controversial nature of this field may be gathered from a few excerpts, chosen at random, from the recent literature: "Platinum salts combine with an enormous number of inorganic and organic groups or molecules and many of these salts have been known for a hundred years, yet the constitution of the isomeric diammines of the type $[PtA_2X_2]$ is still a subject of controversy." (F. H. Burstall, 1938, Annual Reports of the Progress of Chemistry, p. 167.)

"It is still an open question whether the experimental work (relating to planar and tetrahedral structures) has been correctly interpreted or not or whether some elements can assume more than one structure." (J. R. Bailar, 1936, *Chemical Reviews*, **19**, 67.)

"In any event, the problem presented by these salts (certain allegedly optically active platinous salts) does not seem to be finally cleared up." (O. K. Rice, 1940, Electronic Structure and Chemical Binding. McGraw Hill, London and New York, p. 303.)

Although in a certain sense no scientific problem is ever cleared up, I believe that the main outlines of the stereochemistry of bivalent platinum are well established, and that the above quotations, even after due allowance is made for their isolation from their context, scarcely do justice to all the experimental work which has been done in this field.

The stereochemistry of carbon was developed by means of investigations essentially chemical in nature and the results of subsequently developed physical methods were often regarded as merely confirming already well established findings. In the study of platinum compounds however, physical methods have played a much more important role, partly because of their more recent development, but mainly because of certain limitations of the chemical method. Thus the burden of final proof of structure has had to be borne by a number of entirely independent chemical and physical methods of attack and it is to these we shall now turn.

The Discovery of the Square Configuration.

It is not surprising that the square configuration was first discovered among the compounds of Pt^{II}, because, as we now know, no other element forms so many compounds which exhibit isomerism on account of this stereochemical characteristic. The two substances primarily concerned with the development of our knowledge in this field, namely α and β dichlorodiammine platinum, $[Pt(NH_3)_2Cl_2]$, were discovered nearly a century ago, the former by Peyrone (1845) and the latter by Reiset (1844).[1]

The methods used in their preparation involve two similar processes; the α compound is made by replacing two chlorine atoms of the $[PtCl_4]^=$ ion with ammonia molecules, the β by replacing two ammonia molecules of the $[Pt(NH_3)_4]^{++}$ ion with chlorine atoms. The latter operation is effected either by heating solid $[Pt(NH_3)_4]Cl_2$ under carefully controlled conditions or by treating the aqueous solution with concentrated hydrochloric acid: the former by treating K_2PtCl_4 with aqueous ammonia .

There is little doubt that each of the above substitutions proceeds stepwise:

$$[PtCl_4]^{--} \xrightarrow{NH_3} [Pt(NH_3)Cl_3]^- \xrightarrow{NH_3} [Pt(NH_3)_2Cl_2]^\circ$$

$$[Pt(NH_3)_4]^{++} \xrightarrow{Cl^-} [Pt(NH_3)_3Cl]^+ \xrightarrow{Cl^-} [Pt(NH_3)_2Cl_2]^\circ$$

The intermediate compounds have been isolated and each step has been carried out separately.

The problem of explaining the existence of the α and β compounds resolves itself, as a first step, into deciding whether they are

(*a*) isomers (structural or geometrical), or
(*b*) polymers, or
(*c*) dimorphs.

These alternatives, though not explicitly formulated by the earlier workers, can as a result of their work be narrowed down. The last was eliminated first. Cleve (1872), a very active early worker in this field, clearly established the different chemical behaviour of the α and β forms of $[Pt(NH_3)_2Cl_2]$. By treating each form with a series of reagents, including the appropriate silver salts, he prepared and described new (isomeric) compounds such as the α and β forms of

[1] Since their discovery considerable confusion has arisen in regard to their names. They were first known as the chlorides of Peyrone and Reiset respectively and later as plato semi-diammine and platosammine chloride. In 1893 Werner introduced the terms α and β; finally, Drew and his collaborators, for no very good reason, reversed the usage of α and β. In this address Werner's nomenclature will be retained.

$[Pt(NH_3)_2Br_2]$, $[Pt(NH_3)_2I_2]$, $[Pt(NH_3)_2(CN)_2]$, $[Pt(NH_3)_2(NO_3)_2]$ and $[Pt(NH_3)_2(NO_2)_2]$.

Although this and later work leaves no doubt that the α and β forms are not just simply different crystalline modifications of the same substance, it is interesting to note recent confirmation along physical lines. Dimorphous molecular crystals contain the same molecules packed in different ways, so that when each structure is broken down by solution in any given solvent, the resulting solutions should be identical, a point which can, for example, be tested by an examination of absorption spectra (Mellor and Morris, 1938). Small, but definite differences have been noted in the absorption spectra of the aqueous solutions of the α and β $[Pt(NH_3)_2Cl_2]$ (Babayeva, 1938). There is little doubt that, had chemical and physical tests along these lines been carefully applied, many of the issues created by the announcement of an alleged third (γ) form of $[Pt(NH_3)_2Cl_2]$ (Drew, Pinkard, Wardlaw and Cox, 1932*a*) would have been avoided.

If we make the assumption that the coordination number of Pt^{II} is four,[2] and experience has shown this to be practically universal, the number of polymers of empirical composition $[Pt(NH_3)_2Cl_2]_x$ is, for $x > I$, limited to the following:

1. $[Pt(NH_3)_4]$ $[PtCl_4]$ (Magnus, 1828).
2. $[Pt(NH_3)_3Cl]$ $[Pt(NH_3)Cl_3]$ (Peyrone, 1844, 1846).
3. $[Pt(NH_3)_4]$ $[Pt(NH_3)Cl_3]_2$ (Cossa, 1890).
4. $[Pt(NH_3)_3Cl]_2$ $[PtCl_4]$ (Cleve, 1872).

The α and β diammines are distinct from all of these.

Anticipating the discussion in a subsequent section, one may add that, with one rather puzzling exception, molecular weight measurements on α and β forms of compounds of the type $[PtA_2X_2]$ (where $A = NH_3$, Py, $EtNH_2$, etc., and $X = Cl$, Br, CNS, OH, etc.) show that both forms are monomeric.

With the elimination of the possibilities (*b*) and (*c*)—polymerism and dimorphism respectively—the problem now resolves itself into deciding whether the α and β diammines are structural or geometrical isomers. One of the first attempts to understand their constitution was made by Cleve (1872), who proposed structures which, in the light of the then prevailing theories of valency, seemed plausible enough. They were:

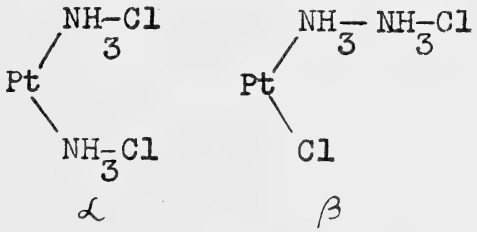


Fig. 2.

[2] Unless this limitation is specified it would be necessary to consider a structure like

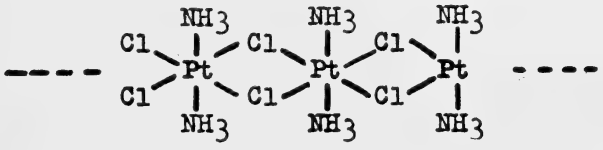


Fig. 1.

There is, however, no evidence for this structure among any platinous compounds of empirical composition $Pt(NH_3)_2Cl_2$.

These formulations which were also supported by Blomstrand, Jorgensen and others, implied, of course, that the substances were structural isomers. With present-day knowledge of atomic structure, which enables an upper limit to be placed on the number of covalent bonds that can be formed by first row elements of the periodic table, these structures can be ruled out immediately, since they both involve five covalent bonds to nitrogen. As will appear in the sequel, there are many other reasons for rejecting them. Nevertheless some attempt was made to revive them a few years ago (Drew *et al.*, 1932*a*) and they are occasionally still seriously discussed in the literature. The revival was the result of an attempt to explain certain reactions of the two compounds but, without going into detail here, it can be stated that all these reactions can equally well be explained on an alternative view of their constitution.

While Cleve's formulations of the two compounds are no longer tenable, they served the very useful purpose in focusing attention on the problem of their constitution. Some fifteen years after Cleve's work, Jorgensen (1886) set out to determine experimentally whether the assignment of the structures to the α and β forms as above had been correctly made or not, and in so doing he laid the experimental foundation upon which one of the most important advances in our knowledge of the structure of platinous compounds was made. This was Werner's introduction of the hypothesis of square coordination. Rejecting all previous explanations in terms of structural isomerism, Werner (1893) applied to the problem those principles which he had so successfully used to account for the constitution of the cobaltic ammines. Realising that, unlike cobaltic ammines, which were universally characterised by a coordination number of six, the compounds of platinous platinum were always four co-ordinated,[3] he put forward the idea that the α and β diammines were geometrical isomers (cis and trans) owing their existence to a planar distribution of the four bonds about the platinum atom as in Fig. 3.

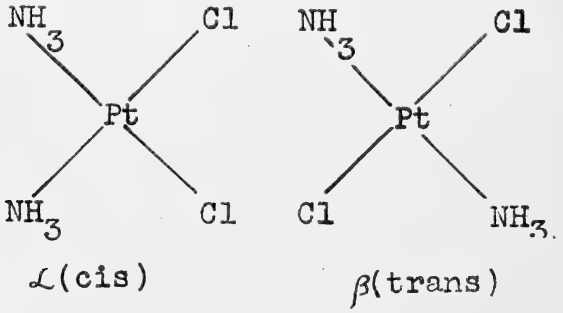


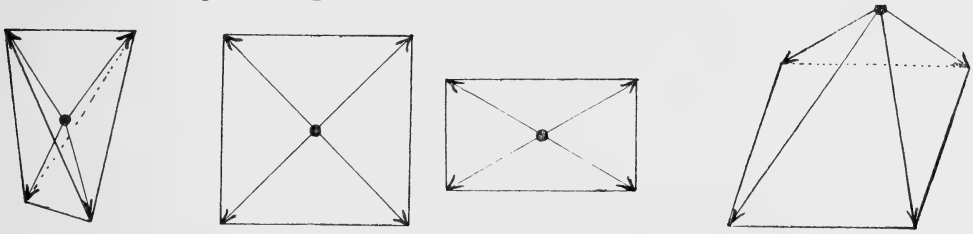
Fig. 3.

With regular tetrahedral bonds from platinum, two isomeric diammines are not possible. Although it would seem that Werner never at any time explicitly stated that the coplanar bonds were directed towards the corners of a square, it is clear from the diagrams of his classical 1893 paper that he considered them to be so directed. He never stressed the size of the bond angles in the plane, presumably because it was not essential in explaining the geometrical isomerism. Actually the term *square* coordination was first used by Pauling (1932) in connection with his quantum mechanical treatment of the directed valence bond.

[3] Some probable exceptions to this statement will be referred to later.

Strictly speaking any one of a number of structures would equally well account for the geometrical isomerism of the α and β dichlorodiammines. The four bonds from platinum might be directed towards :

(1) The corners of a square or rectangle (Fig. 4 (*b*) and (*c*)).
(2) The corners of a pyramid (on a square or rectangular base). Fig. 4 (*d*) shows the first case only.
(3) The corners of a tetragonal or rhombic bisphenoid. (Fig. 4 (*a*) shows the tetragonal bisphenoid.)



(*a*) (*b*) (*c*) (*d*)

Fig. 4.

Each one of these alternatives has been introduced from time to time, to explain the results of some chemical investigation. Thus the third was discussed by Rosenheim and Gerb (1933) in explaining the existence of certain supposedly optically active platinous and palladous complexes. Under the name " paired coordination " it was also used by Drew, Pinkard, Wardlaw and Cox (1932*b*) to account for the isomerism of certain tetrammines. The pyramidal structure (2) was suggested by Dwyer and Mellor (1934) as a means of reconciling results of experiments on mirror image and geometrical isomerism.

It does not seem to have been realised before, that the results of purely chemical methods of investigation do not permit a final decision between alternatives (1), (2) and (3), and that *herein lies the origin of much of the controversy in this field.* To decide between any of these alternatives one must have accurate information about the sizes of the platinum bond angles. Up to the present, chemical methods of investigation (study of composition, isomerism and chemical reactions, etc.) do not enable one to measure the size of these angles. This would seem an inherent limitation of the chemical method of studying molecular structure unless it is able to call on help in the shape of accurately known atomic dimensions derived from physical measurements. This limitation applies, of course, to the classical stereochemistry of carbon, but fortunately for the development of organic chemistry it has not been of great significance. For optical activity to appear in the molecule $CR_1R_2R_3R_4$, all that is required is that the bonds have a general tetrahedral orientation ; there is no need for the bond R_1-C-R_2 to be 109° 28′—it might be 150° or more. It was left to investigators using the techniques of electron diffraction and crystal analysis, etc., to show that the carbon bonds are actually directed to the corners of a *regular* tetrahedron. There may be very rare exceptions to the above statement of the limitations of the chemical method but none has come to light in the chemistry of platinous compounds.

In view of the impasse which thus confronts the chemical method, it would perhaps be more logical now to pass on to the physical methods of studying the problem. This course will not be followed—partly for historical reasons and partly, since the issue has been raised, to show that there is no chemical evidence that permits an unequivocal choice between the above alternatives. The verdict reached in the final summing-up of the physical evidence is that Pt^{II} forms square bonds, a verdict with which the chemical evidence is entirely consistent. In other words, all cases of isomerism in the sections to follow

undoubtedly originate from square bonding, and while this is assumed, throughout it will be seen that any one or other of the three alternatives might equally well have applied.

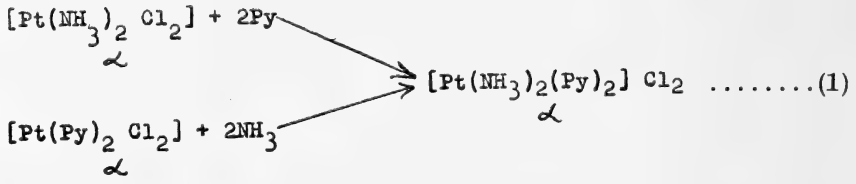
Geometrical Isomerism.

The Determination of the Configuration of the Diammines.

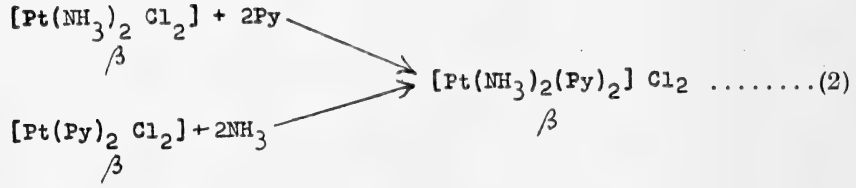
Having decided that the α and β diammines were geometrical isomers, Werner went a step further and by very ingenious reasoning determined which of the two forms was cis and which trans. The reactions concerned (Jorgensen, 1886) may be summarised under two headings :

1. *Addition Reactions.*

When treated with two molecules of pyridine, α dichlorodiammineplatinum forms α diamminedipyridineplatinous chloride. This latter compound can also be prepared by treating α dichlorodipyridineplatinum with two molecules of ammonia :



Similar reactions are observed with β dichlorodiammineplatinum :

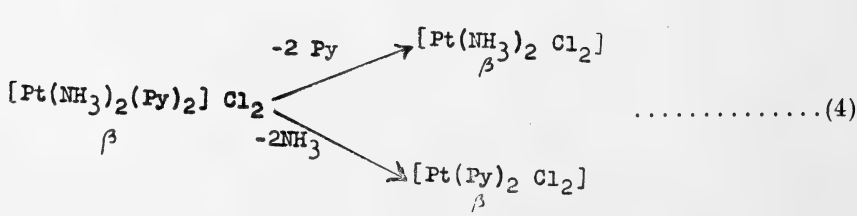


2. *Elimination Reactions.*[4]

By heating the solids alone or by warming aqueous solutions with concentrated hydrochloric acid, the α and β tetrammines revert to the dichlorodiammines. Thus α dipyridinediammineplatinous chloride, when heated, reverts to β dichloropyridineammineplatinum :

$$[Pt(NH_3)_2(Py)_2]Cl_2 \xrightarrow{\alpha} [Pt(NH_3)(Py)Cl_2]_{\beta} + NH_3 + Py \quad \ldots\ldots\ldots \quad (3)$$

On the other hand, β dipyridinediammineplatinous chloride gives rise to a mixture of β dichlorodiammine and β dichlorodipyridineplatinum



[4] These reactions might also be called substitution reactions if we regard them from the point of view of the complex ion only. The names have been used in reference to the molecules as a whole.

The last reaction has been queried by Reihlen and Nestlé (1926), but the experimental work of Jorgensen (1886) and Drew *et al.* (1932*b*) shows that the reaction which takes place is the one formulated. The products were separated by fractional crystallisation and identified by preparing distinctive derivatives. All other addition and elimination reactions have been checked by Drew *et al.*, who used them, not to confirm Werner's hypothesis, but as a basis for the hypothesis of paired coordination links. Suffice it to say that the experimental foundation upon which Werner built his " configuration determination " has stood the test of time.

Whereas Jorgensen was forced to introduce several arbitrary assumptions to account for the above reactions in terms of structural isomerism, Werner was able to account for them in a perfectly straightforward manner with the help of only one further assumption, viz. " trans elimination ". Werner pictured reactions (1) to (4) as proceeding in the following manner (Fig. 5) :

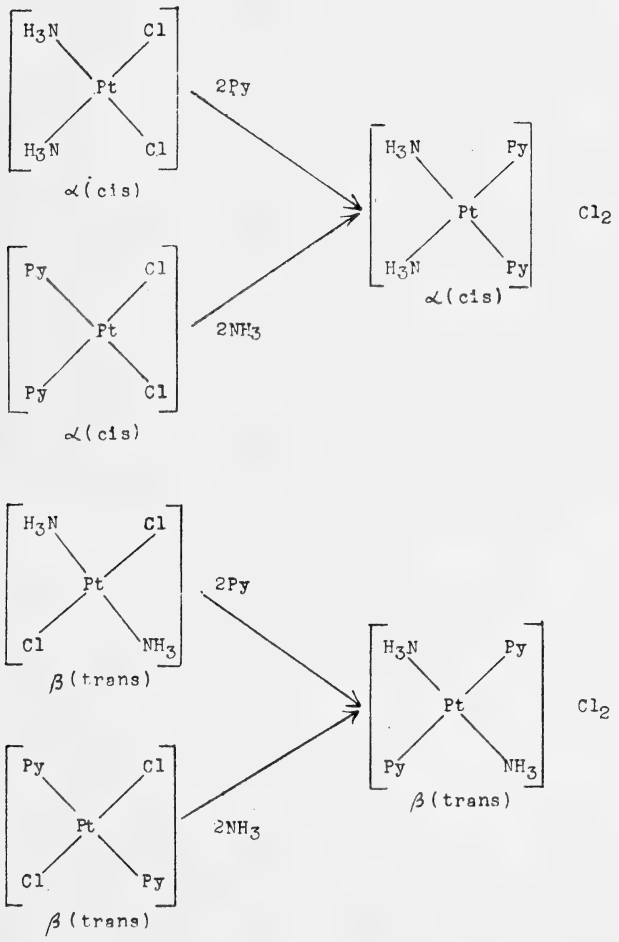


Fig. 5.

In attributing the cis structure to the α compound and the trans structure to the β as above, Werner's final conclusions have been anticipated. His argument in support of this assignment is based on the assumption that, in the

course of the elimination reactions, pairs of groups in *trans positions only* are removed. The results of trans elimination are made clear in the following diagrams where the dotted lines enclose the eliminated trans pairs (Fig. 6).

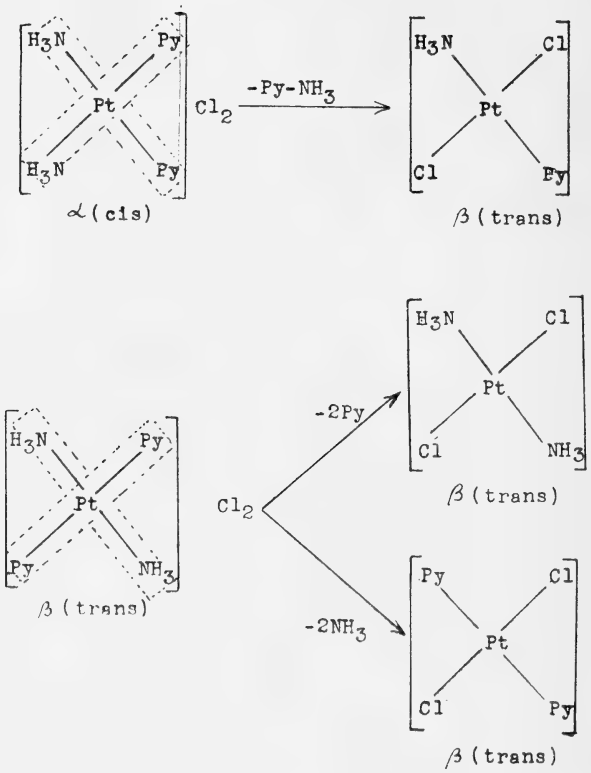


Fig. 6.

An examination of the structure of α (cis) dipyridinediammine platinous chloride will show that elimination of pairs of cis groups should result in the formation of a mixture of three compounds, viz. $[Pt(NH_3)_2Cl_2]$, $[Pt(Py)_2Cl_2]$ and $[Pt(Py)(NH_3)Cl_2]$, whereas actually only one, the last, is obtained. On the other hand, cis elimination from the β (trans) dipyridinediammine complex should result in the formation of only one compound, viz. $[Pt(Py)(NH_3)Cl_2]$; actually two are found: $[Pt(Py)_2Cl_2]$ and $[Pt(NH_3)_2Cl_2]$. If we accept the hypothesis of trans elimination, all the reactions find consistent interpretation in terms of a cis structure for α and a trans structure for β $[Pt(NH_3)_2Cl_2]$.

Such then is the experimental foundation upon which Werner, duly acknowledging his debt to Jorgensen, built the planar hypothesis. Yet nearly forty years later when reviewing this question, Angell, Drew and Wardlaw (1930) remarked: "Werner, ignoring the relevant chemical evidence of his predecessors, (*sic.*) attributed the isomerism to the presence of cis and trans planar types in which platinum exhibited four coordination."

Perhaps the chief weakness in the interpretation of the elimination reactions is that at one stage (elimination from the α (cis) $[Pt(Py)_2(NH_3)_2]Cl_2$) it depends on a negative result—failure to find more than one compound. It is a striking tribute to Werner's remarkable insight into the structure of coordination compounds that all subsequent determinations of the configuration of α and β dichlorodiammine platinum have proved the correctness of his assignment of

cis and trans structures, and at the same time justified his hypothesis of trans elimination—at least for these reactions.

Further Chemical Evidence Confirming Werner's Allocation of Configurations.

With the exception of results from dipole moment studies and from one or two incomplete X-ray crystal analyses, confirmation of Werner's work has been obtained along chemical lines.

In the course of extensive investigations of " ammoniacal platinum bases " Cleve (1872) reported a very interesting difference in the behaviour of α and β $[Pt(NH_3)_2(NO_3)_2]$ towards oxalic acid solution: the α form was converted to a compound with the empirical composition $[Pt(NH_3)_2C_2O_4]$; the β to a compound $[Pt(NH_3)_2(C_2O_4H)_2]$. Some sixty years later Grünberg (1931) confirmed these observations and first suggested their interpretation. In doing so he made use of a method developed by Werner in his study of cis-trans configurations among the octahedral complexes of Co^{III}. Thus Grünberg proceeded on the assumption that the $C_2O_4^=$ group acted as a bidentate chelate only when it replaced two NO_3 groups in cis positions; when it replaced NO_3 groups in trans positions the oxalic acid molecule occupied one coordination position. It is clearly sterically impossible for the $C_2O_4^=$ group to span trans positions if square bonding is to be maintained.[5]

Since the oxalate group enters the α $[Pt(NH_3)_2(NO_3)_2]$ as a bidentate chelate, this form obviously has the cis configuration. Now $[Pt(NH_3)_2NO_3]$

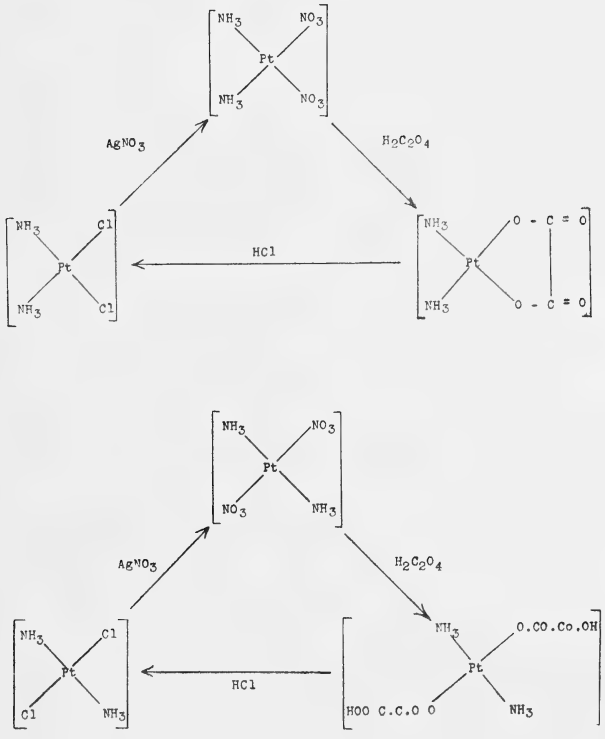


Fig. 7A.

[5] The existence of the so-called trans $PtPy_2SO_4$ would seem to be an exception to this statement. The compound is, however, a dihydrate and is probably $[PtPy_2(H_2O)_2]SO_4$.

is prepared by treating corresponding (α) chloro compound with silver nitrate, and if it be assumed that the substitution of NO_3 for Cl occurs without change of configuration, then α$[Pt(NH_3)_2Cl_2]$ must also be a cis form, in agreement with Werner's contention. That no change of configuration does occur is shown by the behaviour of the oxalate compounds towards hydrochloric acid: the oxalate compound made from cis $[Pt(NH_3)_2(NO_3)_2]$ regenerates cis $[Pt(NH_3)_2Cl_2]$ while the second oxalate compound regenerates the trans dichloro compound. These reactions may be represented schematically (Fig. 7A).

A very similar cycle of reactions has been carried out with α (cis) $[PtPy_2Cl_2]$ (Drew, Pinkard, Wardlaw and Cox, 1932*a*) (Fig. 7B).

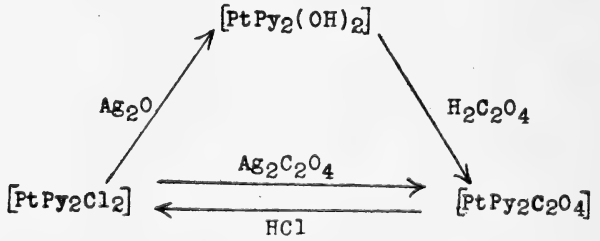
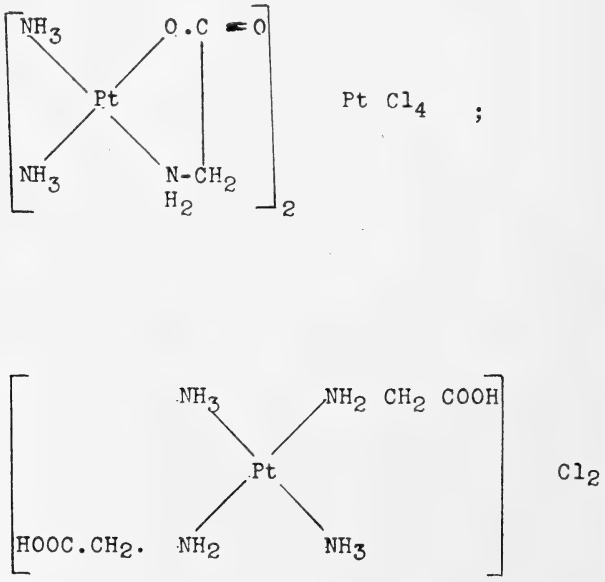


Fig. 7B.

Cis (α) $[PtPy_2Cl_2]$ also reacts with dipyridyl to form $[PtPy_2Dipy]Cl_2$ (Morgan and Burstall, 1934), whereas prolonged boiling of the trans (β) form with alcoholic dipyridyl solution produces no detectable reaction.[6] Passing reference only can be made to other work on the configuration of the dichlorodiammines; further confirmatory evidence is to be found in Grunberg and Ptizyn's (1933) work on glycine complexes (Fig. 8A) and also in some work by Drew (1932),



8A.

[6] Unpublished experiments by the author.

who has shown that α (cis) $[Pt(NH_3)_2Cl_2]$ reacts with ethylenediamine to form $[Pt(NH_3)_2(NH_2 . CH_2 . CH_2NH_2)]Cl_2$ (Fig. 8B), whereas no reaction occurs with the trans form.

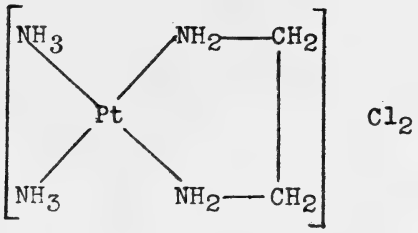


Fig. 8B.

Another method of discriminating between cis and trans $[PtA_2X_2]$ complexes depends on Kurnakow's (1894) test, which is based on the reactions :

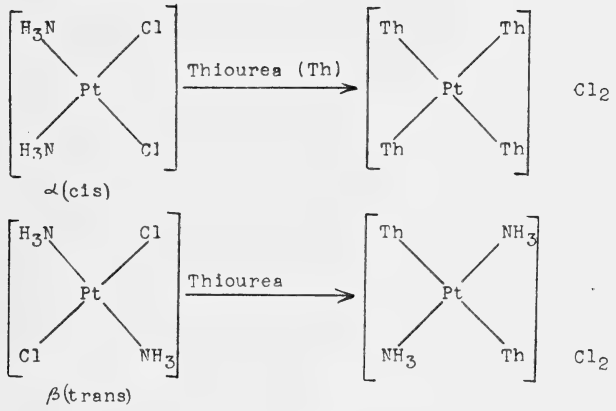


Fig. 9.

These reactions, in themselves, tell one nothing about structure in the sense that the ring closure reactions do. Kurnakow's test has been very frequently used by Russian workers for deciding on the structure of platinous ammines. It would be interesting to know how widely applicable the test is, and it would be worth while to check it against other substances of known configuration such as the thioether, stibine, arsine, and phosphine derivatives.

The Reliability of the Chemical Method of Determining Configuration.

A check on the reliability of the chemical method is afforded by dipole moment measurements which will be dealt with more fully in a subsequent section. Suffice it to say here that confirmatory evidence from this source has been obtained with trans $[PtPy_2Cl_2]$ and with both forms of $[Pt(Et_2S)_2Cl_2]$. The reactions of α $[Pt(Et_2S)_2Cl_2]$[7] reported by Angell *et al.* (1930) show that it has a cis structure ; the measured dipole moment of the compound bears this out. Dipole measurements unfortunately could not be extended to the ammonia complexes owing to their limited solubility in non-polar solvents.

One interesting point emerges from all this work and that is the remarkable stability of platinous complexes. There is no evidence that rearrangement of

[7] This compound is referred to as the β by Angell and his collaborators.

the atoms or groups relative to one another occurs in a complex during chemical reaction, that is, a trans compound retains its trans configuration through a series of reactions. As Wells (1936) has shown, in his study of the structure of $Ag[Co(NH_3)_2(NO_2)_4]$ this constancy of configuration is not characteristic of all complexes. It is certainly not characteristic of square palladous complexes which for some reason, as yet unknown, are not as robust as those of platinous platinum.

Molecular Weight Determinations on PtA_2X_2 Complexes.

Although all the possible polymeric forms of compounds with the empirical composition $Pt(NH_3)_2Cl_2$ have already been discussed, it is necessary to refer to this topic once again, because one of the first criticisms of the theory of square coordination originated in some work on molecular weight determinations (Reihlen and Nestlé, 1926). From a careful study of the vapour pressure lowering in liquid ammonia solutions, Reihlen and Nestlé showed that trans $[Pt(NH_3)_2Cl_2]$ was dimeric in that solvent. At the same time they showed that both forms (cis and trans) could be recovered unchanged from liquid ammonia and proved their technique by measurements on known substances. As the authors themselves point out, the dimerism of the trans form does not prove the square hypothesis false. In spite of this and the fact that Fritzmann (1912) had shown that both forms of $Pt\{Se(C_5H_{11})_2\}_2Cl_2$ were monomeric, Reihlen was so convinced that Werner's interpretation of the structures of the diammines was incorrect that he began a long series of experiments on optical activity, and eventually became one of the chief opponents of the theory of square coordination.

An ebullioscopic determination of the molecular weight of trans $[Pt(NH_3)_2Cl_2]$ in aqueous solution, admittedly not very accurate (Drew, Pinkard, Wardlaw and Cox, 1932*a*) shows it to be monomeric in this solvent. King (1938) has shown that the molecular weights of both forms of $[Pt(NH_3)_2(OH)_2]$ are normal in aqueous solution. As far as other compounds of the type $[PtA_2X_2]$ are concerned there is plenty of evidence that both isomeric forms possess normal molecular weights. One may cite the work of Hantzsch (1926) on α and β $[PtPy_2Cl_2]$, Grunberg (1926) on α and β $[Pt(NH_3)_2(CNS)_2]$, Angell *et al.* (1930) on α and β $[Pt(Et_2S)_2Cl_2]$, and finally the very extensive series of measurements by Jensen (1935*a*) on a wide range of thioether complexes (Table I). All this

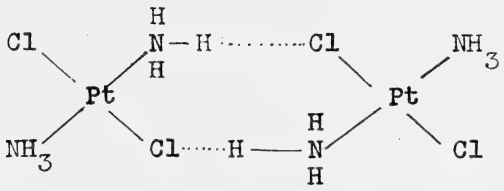
Table 1.

Molecular Weights and Melting Points of Platinous Compounds of the Type $[PtA_2X_2]$. (*After* Jensen, 1935.)

Substance.	Melting Point.	Molecular Weight.	
		Found.	Calculated.
trans $[PtCl_2(Et_2Se)_2]$	60·0	549·0	540·7
cis $[PtCl_2(Et_2Se)_2]$	74·0	618·0	540·7
trans $[PtCl_2(Pr_2S)_2]$	80·0	531·0	502·5
cis $(PtCl_2(Pr_2S)_2]$	85·0	598·0	502·5
trans $[PtCl_2(Bu_2S)_2]$	60·0	564·0	558·4
cis $[PtCl_2(Bu_2S)_2]$	84·5	612·0	558·4
trans $[PtCl_2(i\text{–}Bu_2S)_2]$	110·0	538·0	558·4
cis $[PtCl_2(i\text{–}Bu_2S)_2]$	138·5	672·0	558·4

work leaves no doubt that the cis and trans compounds are monomeric in the solvents used. In Jensen's work there is some evidence of association of the cis forms, but only to a small degree and in keeping with what one would expect from their higher dipole moment. It is interesting to note, too, the effect of the dipole moments on melting points ; of the two, the cis form melts at the higher temperature.

The problem of the dimerism of trans $[Pt(NH_3)_2Cl_2]$ in liquid ammonia still remains. If dipole moment were the principal factor determining association, one would expect the cis form to be the one more associated. Any mechanism of association involving weak hydrogen bonds should operate with



both isomers and might reasonably be expected to cause association beyond the dimer stage. All that can be said at present is that the association of the trans form in liquid ammonia is peculiar to this isomer and to this particular solvent, and, while inexplicable at the present, it does not weaken the theory of square coordination. The importance of the work of Reihlen and Nestlé lies not so much in the peculiarity of the results obtained as in the stimulus it gave to work on the optical activity of platinous compounds to which we shall now turn.

The Mirror Image Isomerism of Platinous Compounds.

If two unsymmetrical chelate groups such as isobutylenediamine are tetrahedrally coordinated to a central metal atom, the resulting complex may exist in mirror image (Fig. 10 (*a*)) but not cis-trans forms. On the other hand, if the

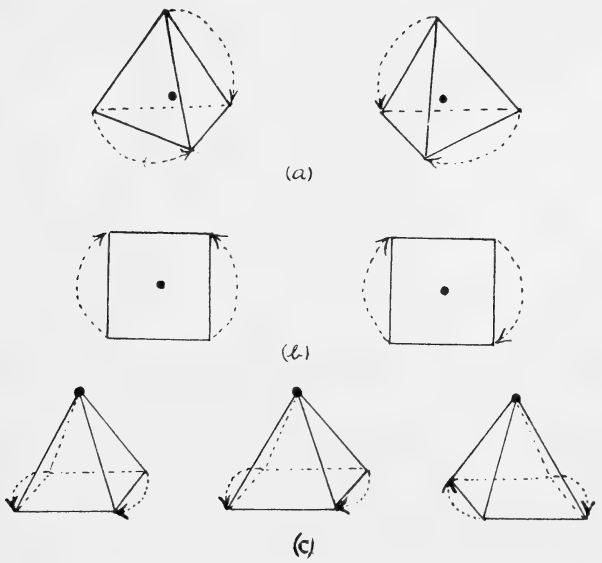


Fig. 10.

chelate groups are coplanar, the complex may exist in cis-trans, but not mirror image forms (Fig. 10 (*b*)). Finally, if Pt^{II} forms pyramidal bonds, both geometrical (cis-trans) and mirror image isomerism are possible ; of the geometrical isomers the trans form only is capable of existing in mirror image isomers. Over a number of years, Reihlen and his collaborators working with various unsymmetrical chelate molecules (see Fig. 10 (*a*)) have made repeated claims that they have obtained evidence proving the tetrahedral configuration of Pt^{II}. Owing to the fact that these claims clash with the main body of evidence, it is necessary to examine them in some detail.

In the first place it must be pointed out that, except in one very doubtful instance, Reihlen and his collaborators have never followed the classical method of establishing a configuration by resolution through to its proper conclusion. That is to say, the allegedly optically active complexes have never been obtained free from the resolving acid (or base).

In one instance (Reihlen, Seipel and Weinbrenner, 1935) where this separation was reported as having been carried out, the observed rotation was so very small (0·06° for a 4 dm. tube) as to be without any special significance. Reihlen's claims, then, rest on the observation that the molecular rotation, [M], of a salt like bis-aminomethyl-3-ethyl-4-methylquinoline platinous α bromocamphor-π-sulphonate (I) (Reihlen and Huhn, 1931) is greater (or less) than that calculated from the α bromocamphor-π-sulphonate content of the salt. All attempts to obtain an optically active complex free from the acid used for resolution resulted in failure which was attributed to racemisation. In view of the stability of platinous complexes, already noted in an earlier section, this explanation is not specially convincing.

Unsuccessful attempts to obtain optically active platinous complexes have been reported by other workers. Ostromisslensky and Bergman (1910) failed with $[PtClNH_3SO_3Py]^-$, Tscherniaev (1928) with $[Pt(NH_2OH)(NH_3)(Py)(NO_2)]^+$, and finally Jensen (1938) with bis thiosemicarbazide and bis-2-aminomethyl-3-ethyl-4-methylquinoline platinous ions. Significantly enough, in the last instance Jensen did note rotation differences of the same order as were observed by Reihlen and Huhn (1931).

However, on attempting to isolate an optically active platinous complex by precipitation with picric acid, Jensen found that the chloroform solution of the resulting picrate was always entirely devoid of optical activity. It is worth noting that several of the compounds upon which attempts at resolution were made have been described in the isomeric forms to be expected from square bonding : thus two forms of bis-isobutylenediamine platinous chloroplatinite (Drew and Head, 1934) and bis-phenylethylenediamine-2-aminomethyl-3-ethyl-4-methylquinoline-platinous chloride (Reihlen, Seipel and Weinbrenner, 1935), and three forms of $[Pt(NH_2OH)(NH_3)(Py)(NO_2)]^+$ (Tscherniaev, 1926, 1928) have been isolated.

In the belief that Reihlen's resolutions were valid, Dwyer and Mellor (1934) suggested a pyramidal structure for the complexes of platinum and palladium with a view to reconciling the findings on optical activity with the known cis trans isomerism. This view is, of course, no longer tenable.

There still remains the question as to what causes the changes in rotation discovered by Reihlen and Jensen. The latter has made the suggestion that the bromocamphorsulphonate molecule becomes attached to the platinum

atom itself, either (1) by forming the complex (*a*)

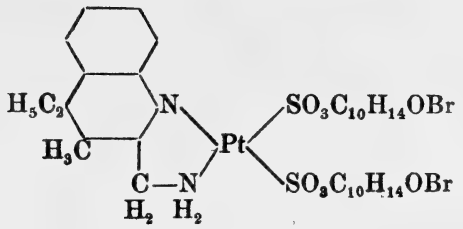


Fig. 11A.

or (2) by opening the chelate rings to form (*b*)

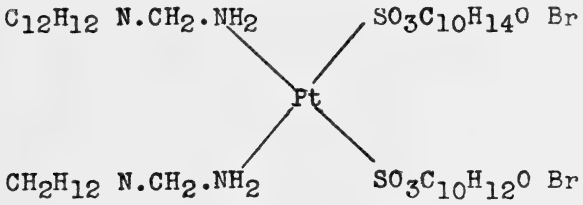


Fig. 11B.

Jensen has calculated that contamination of bis-2-aminomethyl-3-ethyl-4 methylquinoline platinous α bromocamphor π sulphonate (I) with as much as 5% of (*a*) (Fig. 11A) makes so very little difference to the analytical figures that it would not be detected. Formation of the substance (*b*) (Fig. 11B) would not alter the analytical results.

Experiment shows (Jensen, 1938) that on the addition of hydrochloric acid to (I) (which may be contaminated with (*a*) or (*b*) or both), the molecular rotation returns to its normal value, i.e. the value for the free bromocamphor-sulphonic acid. Jensen explains this behaviour as being due to the freeing of the bromocamphorsulphonic acid from (*a*) and/or (*b*).

Whether we accept Jensen's explanation of the rotation changes or not, the fact remains that none of the foregoing optical evidence can be said to favour the view that Pt^{II} is tetrahedrally coordinated. Rather does it constitute negative evidence for alternative structures but such evidence is seldom very convincing because we cannot be certain that the cause or causes of the negative result are exactly what we imagine them to be.

The unsatisfactory situation of the resolution work just described has been largely cleared up by Mills and Quibell (1935), who were the first to describe stable optically active derivatives of Pt^{II}. Unfortunately, as far as the unequivocal proof of the square structure goes, the work of Mills and Quibell on mirror image isomerism leaves us in much the same position as does the work on geometrical isomerism; that is to say their results are quite consistent with the square structure, but they may be explained in terms of other configurations.

Somewhat mistrustful of the work on geometrical isomerism, Mills and Quibell[9] achieved the synthesis of a very ingeniously devised complex which,

[9] "Although the frequency with which isomerism occurs in compounds containing a complex of the type A_2PtB_2 gives great weight to Werner's interpretation, yet it is always difficult in dealing with geometrical isomerism to make certain that the isomerism is actually of the nature supposed. There is no such difficulty with mirror image isomerism." (Mills and Quibell, 1935.)

if planar, would have the symmetry properties required to produce mirror image isomers. As it is drawn in Fig. 12 the molecule possesses neither a plane

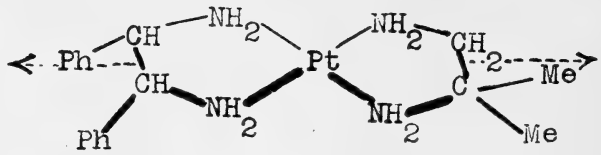


Fig. 12.

nor a centre of symmetry and is therefore resolvable. On the other hand, if the chelate group on the left (stilbenediamine) were fixed, while the chelate group on the right were rotated through 90°, so bringing about a tetrahedral distribution of the four bonds to platinum, the molecule as a whole would possess a plane of symmetry. In other words the molecule with a tetrahedral configuration would no longer be resolvable.

In point of fact, Mills and Quibell were able to isolate, quite free from the resolving acid (d-diacetyltartaric), optically active salts whose great stability is entirely in keeping with what is known of the robustness of platinous complexes. And so for the first time the method of resolution was used to provide evidence for the square configuration. In the light of the general body of evidence, more especially the physical, there is no doubt that these optically active complexes are square, but as Mills and Quibell themselves point out, the results might also have been attributed to a pyramidal arrangement. However, they regarded this last configuration as inherently improbable, pointing out that if it were the explanation of their results, then certain simpler complexes should be resolvable. Inherent improbability is not necessarily a safe argument, as the recent discovery of the pyramidal arrangement of four covalent bonds about Pb^{II} (Moore and Pauling, 1941) will serve to show. For the final stages of the proof of square coordination we must turn to physical methods.

Evidence from Raman Spectra Studies.

In applying Raman spectra to unravelling problems of molecular structure the procedure is, very briefly, as follows: Various molecular models[10] are set up and from symmetry and other considerations the number of Raman lines and their states of polarisation are deduced for each model. These predictions are then compared with the experimental data and that model adopted which gives complete or closest correspondence. It is by no means safe to rely on the number of Raman lines alone in deciding between alternative structures because of the risk that a line, though permitted, may be so faint as to escape detection. The states of polarisation of the lines are just as important as their number and far more difficult to investigate. Nevertheless it is essential that they be determined if reliance is to be placed on the structural conclusions drawn.

As far as square complexes are concerned the simplest Raman spectrum is to be expected from an ion like $[PtCl_4]^=$, which should give three lines, one polarised. Owing to the difficulties associated with work on coloured solutions, K_2PtCl_4 has not been investigated. Mathieu (1939), who has been principally responsible for work in this field, has studied the following colourless (or nearly colourless) compounds $Na_2[Pt(CN)_4]$, $Na_2[Pt(NO_2)_4]$, $[Pt(NH_3)_4]Cl_2$ $[PtPy_4]Cl_2$ and $[Pt(en)_2]Cl_2$. The first compound only gave results upon which a structural decision could be made. Assuming that the three atoms PtCN are collinear,

[10] The number and polarisation of fundamental vibrational Raman lines expected for many common types of molecules have been tabulated by Hibben (1939); square complexes have not been included in this scheme.

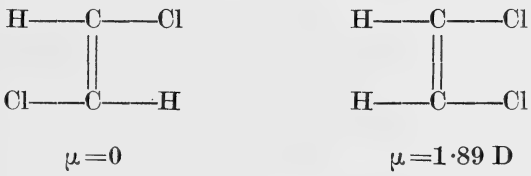
and crystal structure work supports this assumption, the $[Pt(CN)_4]^=$ ion should give either (1) eight lines, for two of which $\rho\left(\frac{i}{H}\right)=0$, if tetrahedral, or (2) seven lines, two of which are polarised, if square. Six lines, one very faint, were in fact observed and of these two were polarised ($\rho\sim0{\cdot}35$).

" Without attempting to study in detail the assignment of the lines to the different modes of vibration one concludes immediately that the experimental results obtained in the case of the tetra-cyanide are compatible only with the square structure " (Mathieu, 1939). The evidence thus rests on the state of polarisation of two lines, since the total number of lines observed was less than that required by either the square or tetrahedral model.

Besides excluding the tetrahedral structure, the Raman spectrum of $[Pt(CN)_4]^=$ also rules out the possibility of a rectangular complex ($Pt<\neq90$), but whether it also rules out the pyramidal structure has not yet been investigated. Evidence in regard to the elimination of this last configuration is to be found in dipole moment and crystal structure studies.

Evidence from Dipole Moments.

Whereas all diatomic molecules of the type A—A are electrically symmetrical and non-polar, those of the type A—B always have a permanent electric moment. In a polyatomic molecule, each bond A—B is associated with a dipole moment which can be treated as a vector quantity, the permanent dipole moment of the molecule as a whole being the vector sum of the individual bond moments. For any molecule with a centre of symmetry, the vector sum of the bond dipole moments will be zero, that is, the molecule will have no permanent dipole moment. This is found to be true of a number of molecules whose structures have been ascertained by other means; CO_2 (linear), BCl_3 (planar triangular), and $SnCl_4$ (tetrahedral) and SF_6 (octahedral) are all centro-symmetrical and without a permanent dipole moment. Of the two isomeric dichloroethylenes, for example, the trans form only is non-polar.



$\mu=0$ $\mu=1{\cdot}89$ D

Fig. 13.

Other instances could be given but these will suffice to indicate the reliability of the method of using dipole moment measurements in testing for centro-symmetry.[11]

Among the dipole studies of metal complexes those of Jensen (1935*a*, 1936*a*) dealing with isomerides of the type $[PtA_2X_2]$ have an important bearing on the present discussion. The results of some of Jensen's measurements are set out in Table 2, from which it can be seen that the compounds fall into two groups. In the first, where A is represented by various symmetrically substituted arsines, phosphines, and stibines, and X by NO_2, Cl, Br, etc., the moments are either approximately zero or around 8-12 Debye units. The compounds with zero moment are obviously the trans forms and those with the large moment, the cis forms. In $[PtCl_2((CH_3)_3As)_2]$, for example, the resultant of the three

[11] Whilst a vanishingly small permanent dipole moment proves the presence of a centre of symmetry in a molecule, it should be borne in mind that, occasionally, a small permanent dipole moment is found in molecules which are on other grounds believed to be centrosymmetrical.

TABLE 2.

Dipole Moments of Platinous Compounds of the Type PtA_2X_2.
(Jensen, 1936.)

Compound.	Dipole Moment. (Debye Units.)	Compound.	Dipole Moment. (Debye Units.)
trans $[PtBr_2(Et_3P)_2]$ ..	0	cis $[PtBr_2(Et_3P)_2]$ ..	11·2
trans $[PtI_2(Et_3P)_2]$ ..	0	cis $[PtI_2(Et_3P)_2]$ ..	8·2
trans $[PtCl_2(Pr_3P)_2]$ ..	0	cis $PtCl_2(Pr_3P)_2$	11·5
trans $[PtCl_2(Et_3As)_2]$ ..	0	cis $[PtCl_2(Et_3As)_2]$ ..	10·5
trans $[PtI_2(Et_3Sb)_2]$ ..	0	cis $[PtCl_2(Et_3Sb)_2]$ ..	9·2
trans $[PtCl_2(Bu_3P)_2]$ ..	0	cis $[PtCl_2(Bu_3P)_2]$ ..	11·5
trans $[PtCl_2(Pr_2S)_2]$ ..	2·35	cis $[PtCl_2(Pr_2S)_2]$ ..	9·5
trans $[PtCl_2(Bu_2S)_2]$ ..	2·35	cis $[PtCl_2(Bu_2S)_2]$ ..	9·2
trans $[Pt(NO_2)_2(Pr_2S)_2]$ ..	2·48	cis $[Pt(NO_2)_2(Pr_2S)_2]$ ..	13·1
trans $[PtBr_2(Et_2S)_2]$ ..	2·26	cis $[PtBr_2(Et_2S)_2]$ ..	8·9

As—C bond moments is directed along the Pt—As bond irrespective of whether there is or there is not rotation about the Pt—As bond. The only reasonable structure for $[PtCl_2((CH_3)_3As)_2]$ which could give zero moment is the trans planar (Fig. 14A).

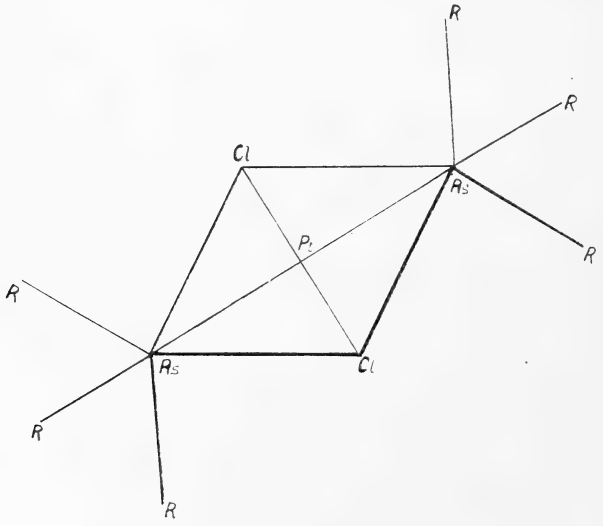


Fig. 14A.

In the second group, which comprises the thioether complexes, there is a large difference between the α and β forms, the dipole of neither form being zero.

However, it is concluded that the compounds with the larger moments are the cis forms and those with the smaller the trans forms. If we make the reasonable assumption that in trans $[Pt(Et_2S)_2Cl_2]$ the platinum bonds are coplanar, the small moment of the molecule can be accounted for in terms of the known configuration of tercovalent sulphur. Indeed the moment of the trans form may be looked upon as supplying further proof that the three sulphur valences are not coplanar. The diagram (Fig. 14B) will make it clear that the S—C moments are not directed along the direction of the Pt—S bond, and that the molecule as a whole must have a resultant dipole moment.

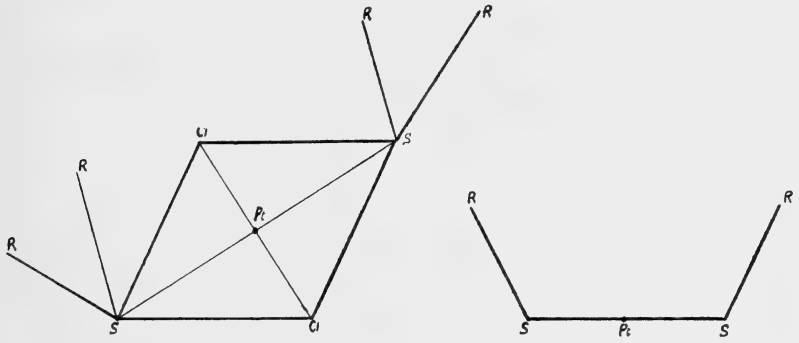


Fig. 14B.

Jensen's work provides a neat physical method for determining the configuration of metal complexes and at the same time it confirms the results of chemical methods of attack on this problem. More important still, it shows that the complexes are strictly planar, and in fact constitutes one of the strongest pieces of evidence against any suggestion of a pyramidal configuration. From the relevant dipole data it is estimated that the platinum atom cannot, at most, be more than 0·08 A from the plane of the four attached groups. Dipole measurements do not tell us what the magnitudes of the $Pt\begin{matrix}>Cl\\<As\end{matrix}$ bonds angles are, and hence do not enable us to say whether the coordination is square $\left(Pt\begin{matrix}<Cl\\As\end{matrix}\cong 90°\right)$ or not. Departures from angles of 90° do not disturb the centrosymmetry of the complex, the minimum requirement to account for a dipole moment of zero. For proof of square as against rectangular coordination we must consider the findings of X-ray analysis of crystals.

The Crystal Structure of Platinous Compounds.

When based on sufficient reliable intensity data and carried through to completion, X-ray crystal analysis may be looked upon as a final court of appeal in structural problems. Often, however, a crystal may be so complicated and the difficulties associated with its determination so great that only a partial solution can be obtained. Evidence from crystal structure analyses must therefore be given varying weight according to the completeness of the analysis, always assuming of course that each stage has been reliably determined. Several stages in an analysis may be recognised : (1) the determination of the size of the unit cell and the number of molecules contained therein. As a rule the number of molecules per unit cell determines to a large extent the complexity of a structure. If there happen to be a large number of molecules, in themselves fairly complicated, the task may prove extremely difficult, if not impossible, at this stage of the development of X-ray technique. An investigation terminated

at the first stage is of little use, although on several occasions attempts have been made to use the fact that one of the dimensions of a unit cell is very small, to prove the existence of some planar structure. Conclusions based on such slender evidence must be accepted with caution, because a small cell dimension may be explained in some other way.[12]

(2) The second stage leads to the determination of the space group which describes fully the symmetry of the crystal structure. Once the number of molecules per unit cell and space group have been determined, it is possible to state the symmetry elements of the molecule itself. By these means, the following molecules (or ions) have been shown to have a centre of symmetry.

(*a*) Bis salicylaldoxime platinum (Cox, Pinkard, Wardlaw and Webster, 1935*c*).
(*b*) Bis dimethylsulphine dichloro platinum (Cox, Saenger and Wardlaw, 1934*a*).
(*c*) Bis ethylenediamine platinous ion (Cox and Preston, 1933).

In all these instances centrosymmetry is consistent with trans planar structures for the complexes, but not with tetrahedral structures.

(3) The third and final step involves finding the exact location of each atom in the unit cell, and as a rule this becomes increasingly difficult as the number of parameters required to fix these positions increases. Relatively few complete structure determinations have been made on platinous compounds and they have, for the most part, been confined to relatively simple structures. Nevertheless the results are of great stereochemical interest. The structures of the following substances have been completely determined and in every instance square complexes have been found :

(1) K_2PtCl_4 (Fig. 15).
(2) $[Pt(NH_3)_4]Cl_2H_2O$ (Fig. 16).
(3) K_2PtCOS_4 (Fig. 17).
(4) $PtC_{32}H_{16}N_8$.
(5) PtS (Fig. 18).

The first substance examined was K_2PtCl_4 (Dickinson, 1922), which together with K_2PdCl_4 belongs to the tetragonal system and has one molecule per unit cell. Because K_2PtCl_4 and $[Pt(NH_3)_4]Cl_2$ form the starting materials for the preparation of many of the isomeric ammines discussed earlier and in this sense are key substances, their structure will be discussed in detail.

K_2PtCl_4 possesses an unusually simple structure, involving as it does but one parameter, a parameter to fix the position of the chlorine atom in the plane of the platinum atoms as shown in the accompanying figure. The positions of the potassium and platinum atoms are fixed uniquely by symmetry.

In the absence of any crystal faces indicating the contrary, Dickinson assumed that the crystal belonged to the holohedral class and his final structure determination in a sense justified this assumption. Nevertheless it is always useful to have some independent evidence of the absence of lower symmetry in the crystal. Such has been provided by piezoelective tests (Theilacker, 1937) and pyroelectric tests (Mellor and Quodling, 1935), both of which show that the crystal does not lack a centre of symmetry.

The isomorphous palladium compound has been reinvestigated with more recently developed X-ray technique by Theilacker (1937) and Dickinson's (1922) earlier work completely confirmed. From his intensity data Theilacker concludes

[12] Because one of its cell dimensions is small as compared with others it has been suggested (Cox *et al.*, 1937*a*) that the compound $CoPy_2Cl_2$ contains square coordinated Co^{II}. Magnetic evidence is against this suggestion, and the small cell dimension can be explained on the basis of an octahedral structure (Mellor and Coryell, 1938).

that the palladium atom cannot, at most, be more than 0·2 A. out of the plane of the four chlorine atoms, and that since this is not much greater than the experimental error it is practically certain that all five atoms are strictly co-planar. Certainly all the evidence on the symmetry of the crystals points to

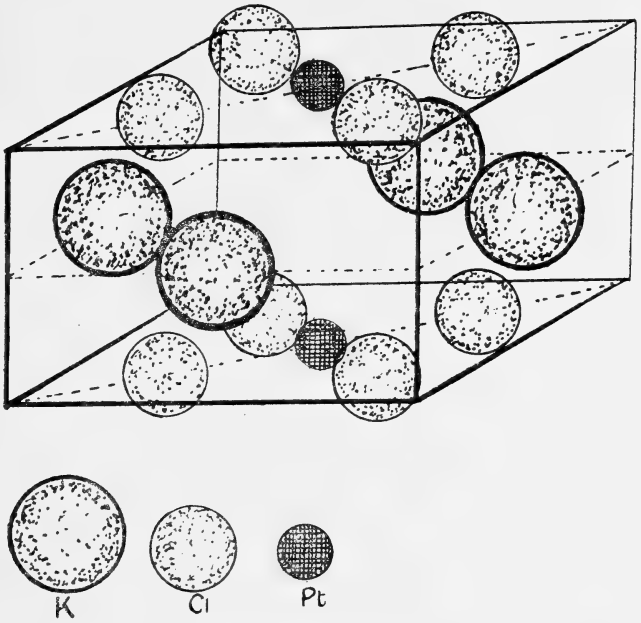


Fig. 15. $K_2[PtCl_4]$.

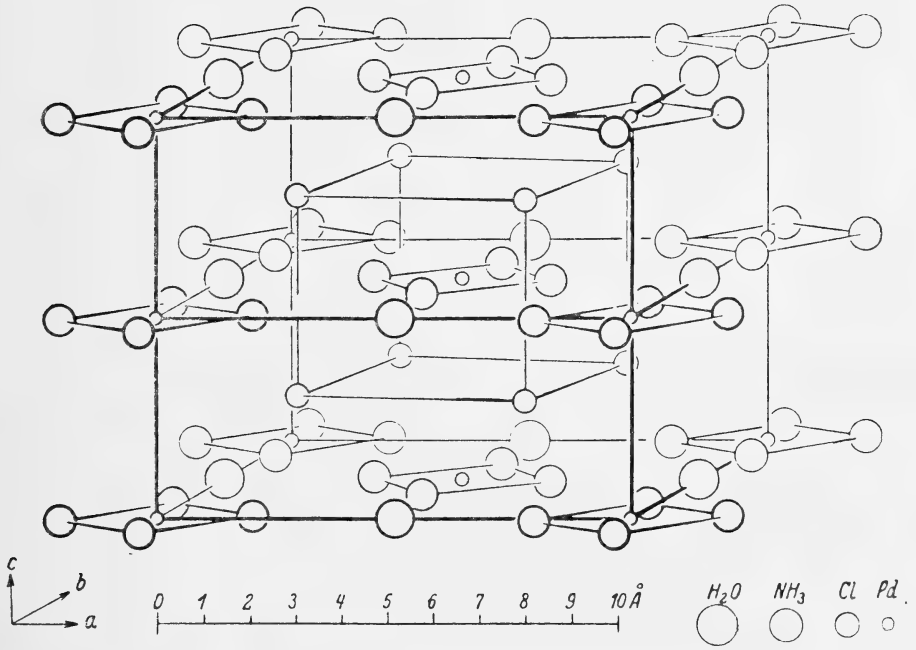


Fig. 16. $[Pd(NH_3)_4]Cl_2H_2O$ and $[Pt(NH_3)_4]Cl_2H_2O$ (Strukturbericht).

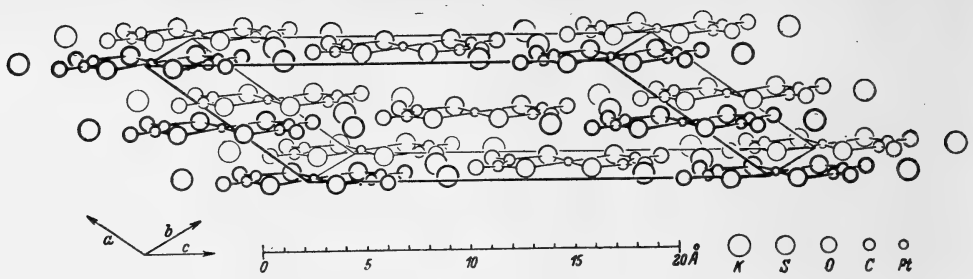


Fig. 17. $K_2[Pt(COS)_4]$ (Strukturbericht).

this conclusion. If it is accepted, then it follows immediately from the tetragonal symmetry of the crystal that the four Pt-Cl bonds are at exactly 90°, and that the $[PtCl_4]^=$ complex is definitely square. The stereochemical implications of this crystal structure determination were not at first fully realised. They are, however, most important, because for the first time accurate information of the orientation of the four platinum bonds became available. One or two additional points about the structure are worth noting. Firstly, the strong negative double refraction of the crystal (Mellor and Quodling, 1935) is consistent with the structure attributed to it. Several small discrepancies between observed and calculated intensities in Dickinson's work on K_2PtCl_4 can be explained on the basis of the anisotropic thermal motions of the platinum atoms (Helmholtz, 1936). However the thermal oscillations of platinum atoms are about fixed mean positions so that no modification of the square structure is required.

The second relatively simple compound, $[Pt(NH_3)_4]Cl_2H_2O$, was first investigated by Cox (1932), who assigned to it a structure the same in essentials as K_2PtCl_4– with the two Cl^- ions occupying the positions of the $2K^+$ ions and the $[Pt(NH_3)_4]^{++}$ that of $[PtCl_4]^=$.

Subsequent work has shown that while the essential features of the $[Pt(NH_3)_4]^{++}$ complex are as Cox reported them (the four platinum valences coplanar and directed towards the corners of a square), the structure of the crystal is a little more complicated, requiring for its proper description a two-molecule unit cell (Dickinson, B.N., 1934).[13] The two molecule cell arises from the small rotations of the $[Pt(NH_3)_4]^{++}$ complexes and chlorine atoms about the " c " axis (Fig. 16). Robertson and Woodward's (1940) analysis of platinous phthalocyanine is one of the most extraordinary X-ray analyses carried out to date, but it adds little to the general theme developed here. The phthalocyanine molecule is a huge planar molecule and any metal atom attaching itself to it by the four pyrrole nitrogen atoms must do so by coplanar bonds.

In the crystals so far mentioned the complexes have all belonged to the finite class. In the last crystal of the group, viz. PtS (Bannister and Hey, 1932) we find a new type—an infinite complex extending throughout the crystal in three dimensions. Platinum and sulphur maintain a coordination number four by appropriate *sharing* of atoms ; portion of an infinite chain structure can be seen in the unit cell of PtS shown in Fig. 18.

Finally we come to several structures which have not been directly determined but which may be inferred from the complete crystal analysis of an isomorphous crystal. Square coordinated metal complexes are found in each,

[13] Dickinson's most detailed work actually related to the isomorphous palladous compound $Pd(NH_3)_4Cl_2 . H_2O$.

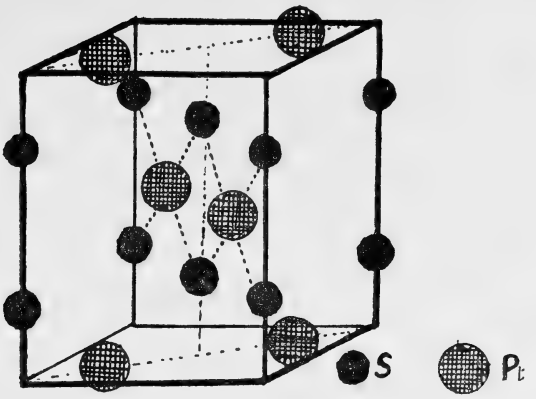


Fig. 18. PtS.

and it must suffice merely to list them with the completely analysed crystal indicated in brackets :

(*a*) $BaPt(CN)_4 4H_2O$($BaNi(CN)_4 4H_2O$) (Brasseur and de Rassenfosse, 1938).
(*b*) $Na_2Pt(CN)_4 3H_2O$($Na_2Ni(CN)_4 3H_2O$) (Brasseur and de Rassenfosse, 1941).
(*c*) $PtCl_2$($PdCl_2$) (Wells, 1938).
(*d*) PtO(PdO) (Moore and Pauling, 1941).

Some Optical Properties of the Crystals of Platinous Compounds.

Taken by itself, evidence from crystal optics is not specially significant, but in conjunction with other data it may often afford valuable confirmation of the existence of certain structural features in a crystal. It is interesting to recall that von Laue's discovery of the diffraction of X-rays upon which the science of crystal analysis was built, was in no small measure conditioned by Ewald's theoretical studies of the double refraction to be expected from certain postulated atomic arrangements in crystals. The science of crystal analysis has amply repaid this debt by providing such a wealth of information about atomic arrangements as to enable the formulation of useful correlations between structure and optical properties.

The striking double refraction of crystals of the isomorphous series $CaCO_3$, $NaNO_3$ and $ScBO_3$, for which the presence of parallel planar XO_3 ions is responsible (Bragg, 1924), suggested that similar optical properties would be found among crystals containing square coordinated Pt^{II}.

According to the results of X-ray analysis the square $[PtCl_4]^=$ groups in K_2PtCl_4 are all arranged parallel to 001. If this arrangement is correct the crystal should show strong negative double refraction, which indeed it does (Mellor and Quodling, 1935). Had the four chlorine atoms been tetrahedrally arranged about the platinum, one would have anticipated a small double refraction of the same order as that found in crystals containing $SO_4^=$, $PO_4^{\equiv}$, ClO_4^-, etc.

Information about the crystal optics of other platinous compounds is summarised in Table 3, from which it can be seen that throughout, the double refraction is high. The high double refraction of Zeise's salt ($K[PtC_2H_4Cl_3]$) is interesting ; it is not known just how the ethylene is incorporated in the complex but the complex undoubtedly has a square configuration.

The strength of the double refraction of a crystal will depend on mutual arrangement of any anisotropic units it may contain, being greatest, and negative, when they are all parallel to one another as in $CaCO_3$ and K_2PtCl_4. Certain arrangements of planar groups result in positive double refraction, as in bastnæsite (Wooster, 1938) ; with other arrangements, less probable no doubt, it

TABLE 3.

The Birefringence of Some Platinous Compounds.

Substance.	Symmetry.	ω_D α_D	β_D	ε_D γ_D	Double Refraction.
$K_2[PtCl_4]$[1]	Tetragonal.	1·683	—	1·553	−0·130
$Ba[Pt(CN)_4]4H_2O$[2] ..	Monoclinic.	1·6706	1·677	1·8982	+0·2276
$Mg[Pt(CN)_4]7H_2O$[3] ..	Tetragonal.	1·561	—	1·910	+0·350
$LiK[Pt(CN)_4]3H_2O$[4] ..	Orthorhombic.	1·6237	1·6278	2·2916	+0·6679
trans $[PtPyNH_3Cl_2]$[5] ..	Triclinic.	1·653	1·732	>1·79	>−0·137
cis $[PtPyNH_3Cl_2]$[5] ..	?	1·624	1·732	>1·79	>−0·166
$K[PtCl_3C_2H_4]H_2O$[6] ..	Monoclinic.	<1·627	—	1·717	>−0·090
$NH_4[PtCl_3C_2H_4]H_2O$[6] ..	Monoclinic.	<1·623	—	1·702	>? 0·079
$Na_2[Pt(CN)_4]3H_2O$[9] ..	Triclinic.	—	—	—	High and negative.
$Sr[Pt(CN)_4]5H_2O$,[7] ..	Monoclinic.	1·547	1·613	1·637	−0·090
$K_2[Pt(COS)_4]$[8]	Monoclinic.	—	—	—	Extremely high.

[1] Mellor and Quodling, 1935. THIS JOURNAL, **69**, 167.
[2] Winchell. "The Optic and Microscopic Character of Artificial Minerals", No. 4, p. 15. Univ. Wisconsin Studies in Science, 1475.
[3] Gaubert, 1917. *Bull. Soc. Fr. Min.*, **40**, 177.
[4] Winchell. *Ibid.*, p. 20.
[5] Gelman, 1939. *C.R. Acad. Sc. U.R.S.S.*, **22**, 107.
[6] Jorgensen, 1900. *Z. anorg. Chem.*, **24**, 153.
[7] Brasseur and de Rassenfosse. *Mem. Acad. Roy. Belg.*, **16**, 1.
[8] Cox, Wardlaw and Webster, 1935. *J. Chem. Soc.*, 1475.
[9] Brasseur and de Rassenfosse. *Ibid.*, 1941 [2], **4**, 397.

is conceivable that a very low double refraction could be produced. Thus, while high double refraction undoubtedly indicates the presence of highly anisotropic units in a structure, low double refraction does not necessarily mean that such units are absent. In this connection another situation which may arise must be kept in mind. Double refraction is subject to dispersion, that is, it varies with wave length and one may just happen to choose, for making a measurement, a wave length where the double refraction is low or at a minimum. This point is well brought out in Brasseur and Rassenfosse's recent (1937 and 1941) extensive studies of the crystal optics of a whole series of complex cyanides of the types $Ba[Me(CN)_4]4H_2O$, $CaMe(CN)_45H_2O$, $Sr[Me(CN)_4]4H_2O$ and $Na_2[Me(CN)_4]3H_2O$ where Me=Pt, Pd and Ni. Without exception, these substances show high double refraction, and for all except three, $BaPt(CN)_44H_2O$, $Mg[Pt(CN)_4]7H_2O$ and $Ca[Pt(CN)_4]5H_2O$, the sign of the double refraction is negative. A complete crystal structure analysis of $BaNi(CN)_44H_2O$ reveals a structure which accords with high negative double refraction. The positive sign of the isomorphous platinum compound is an extremely puzzling anomaly for which no explanation has yet been given. There is little doubt about the observations on the positive sign since the same results have been reported by several workers. It would seem that Bragg's theory of the origin of double

refraction of planar complexes needs further refinement if it is to take account of these platinum compounds.

Magnetic Anisotropy.

Practically nothing has been done on the diamagnetic properties of platinous compounds, but it can reasonably be expected that like $CaCO_3$, $NaNO_3$, etc., they will show pronounced anisotropy. Some very early observations on $Ca[Pt(CN)_4]5H_2O$ were made by Grailich (1858), who reported that the direction of greatest diamagnetic susceptibility is parallel to the " c " axis of the (orthorhombic) crystal. This would place the plane of the $[Pt(CN)_4]$ group approximately perpendicular to the " c " axis, whereas the optical properties suggest a different orientation. The crystal optics of the isomorphous nickel compound, $Ba[Ni(CN)_4]4H_2O$, place the plane of the $[Ni(CN)_4]$ group approximately parallel to the " c " axis in qualitative agreement with the observations on the diamagnetic anisotropy of the platinum compound. Further work, possibly along the lines of that of Born (1923) and Hylleraas (1927) on quartz and calomel, is needed to clear up the anomalous behaviour of these platinum compounds.

Some Reactions of Square Complexes.

Trans Elimination.

In the light of the crystal structure determinations of K_2PtCl_4 and $[Pt(NH_3)_4]Cl_2H_2O$ it is of interest to note at this stage certain features of the reactions involved in the formation of the isomeric diammines. The most important of these is the process of trans elimination discovered by Werner. So far little has been done towards providing a satisfactory understanding of this phenomenon, and all that will be attempted here will be to formulate some of the problems that arise. At the outset it is obvious that trans elimination cannot be a perfectly general reaction, because although it provides an explanation of some of the transformations, cis elimination must be invoked to explain others.

Let us consider first the reaction responsible for the discovery of trans elimination

$$[Pt(NH_3)_4]^{++} \xrightarrow{2HCl} \underset{\text{trans}}{[Pt(NH_3)_2Cl_2]}$$

If we regard the elimination of the two molecules of ammonia as occurring simultaneously, we might suppose that as the two trans molecules depart two chlorine atoms enter the trans octahedral positions to form a new trans square complex, as shown in the accompanying diagram.

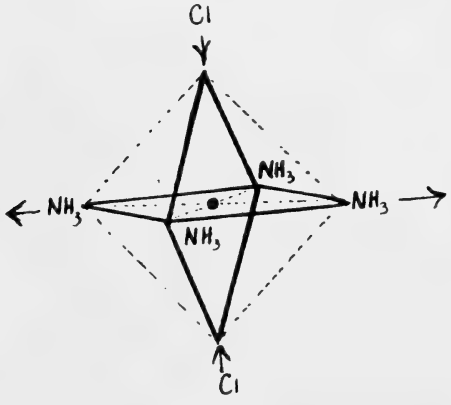


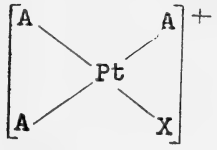
Fig. 19.

But matters are not so simple as this. As already pointed out, the two reactions below proceed stepwise:

$$[Pt(NH_3)_4]^{++} \xrightarrow{Cl^-} [Pt(NH_3)_3Cl]^{+} \xrightarrow{Cl^-} [Pt(NH_3)_2Cl_2]_{\beta}$$

$$[PtCl_4]^{=} \xrightarrow{NH_3} [PtNH_3Cl_3]^{-} \xrightarrow{NH_3} [Pt(NH_3)_2Cl_2]_{\alpha}$$

If the complexes were tetrahedral it would be impossible to account for the two different end products of these reactions. Let us imagine we have a square complex



into which another X is to be substituted for one of the A's. In what circumstances does the first X group direct the second one entering, to the cis position as in $[PtNH_3Cl_3]^-$ or to the trans position as in $[Pt(NH_3)_3Cl]^+$? At first sight it might seem as though X groups are trans directing when present in cationic complexes. Pinkard, Saenger and Wardlaw (1933) have studied very thoroughly the elimination reactions occurring with tetrammines containing ammonia, pyridine and hydroxylamine, and in every instance the reaction indicates trans elimination. (See Fig. 20.) It will be seen that no other X group than Cl was investigated, and as far as the author is aware no systematic work has been done on this point. In this connection the behaviour of certain nitro palladium compounds is worthy of note. From the evidence available (Mann *et al.*, 1935*b*) it would seem that NO_2^- group is cis directed when it enters the complex $[Pd(NH_3)_3NO_2]^+$ and trans directed when it enters the complex $[Pd(NH_3)(NO_2)_3]^-$, which is just the opposite of the behaviour of chlorine in the above platinum complexes.

Two examples will suffice to show that the charge on the complex as a whole is not the factor determining directive influences. When $[Pt(NH_3)_2dipy]Cl_2$ is treated with hydrochloric acid, the cis ammonia molecules are eliminated. This is perhaps hardly a fair test case because if ammonia molecules are to be eliminated there is no choice, but cis elimination. A more convincing case is the one discovered by Jensen (1935*a*) who, in the course of his dipole moment investigations, found that when an aqueous solution of K_2PtCl_4 is treated with four molecules of triethylphosphine, a colourless solution of $[PtP(C_2H_5)_3{}_4]Cl_2$ is formed. This solution on standing deposits cis $[Pt(P(C_2H_5)_3)_2Cl_2]$ ($\mu = 10{\cdot}7$ D) and the only way this latter substance can be formed is by cis elimination from $[PtP(C_2H_5)_3{}_4]Cl_2$.

Cis Elimination.

The reaction between ammonia and the $[PtCl_4]^=$ ion seems typical of many amines. Cis elimination from this ion is known to occur with ethylamine, pyridine, hydroxylamine, aniline, etc., but again the reaction is not a perfectly general one. Some very interesting work in this field has been published by Tscherniaev and his school (Tscherniaev and Gelman, 1936; Gelman and Bauman, 1938). One of their most important findings is that *order* of substitution plays an important part in some complexes. Thus it was found that when ethylene is passed through Cossa's potassium salt, $K[Pt(NH_3)Cl_3]$, cis $[Pt(NH_3)(C_2H_4)Cl_2]$ is formed. On reversing the order of introduction of the

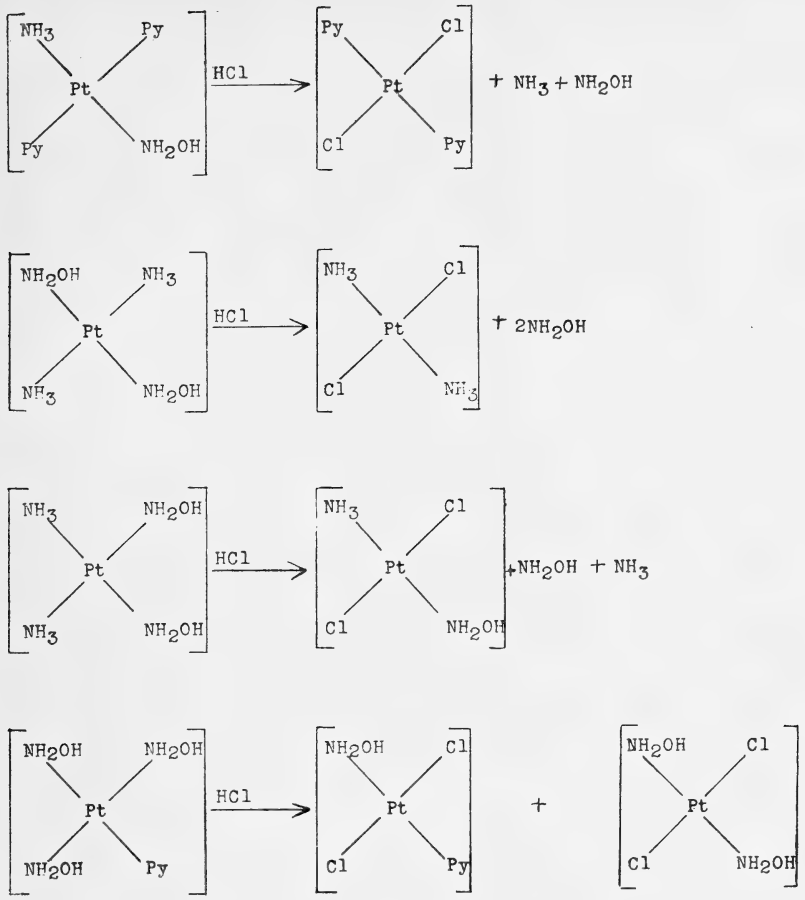


Fig. 20.

groups, i.e. by treating Zeise's salt, $K[PtC_2H_4Cl_3]$, with ammonia trans $[Pt(NH_3)(C_2H_4)Cl_2]$ is formed. Similar behaviour was observed on substituting carbon monoxide for ethylene but the effects of ordered substitution are confined to unsaturated substances like ethylene and carbon monoxide. It does not, for example, make any difference whether $K[PtPyCl_3]$ is treated with ammonia or $K[Pt(NH_3)Cl_3]$ with pyridine, cis $[PtPy(NH_3)Cl_2]$ is the result. These instances are sufficient to show that the directive influences in substitution in square complexes present an interesting problem for the theoretical chemist.

The Universality of the Square Structure among Platinous Compounds.

It now remains to consider whether the square structure is universal among Pt^{II} compounds and as characteristic of that atom as the tetrahedral structure is of carbon. The cases put to the test in physical investigation are necessarily few in number. As there is now no doubt about the origin of the geometrical isomerism, a better idea of the extent of the occurrence of the square structure can be gained from a brief survey of isomeric forms. Final warrant for extrapolating to cover all platinous compounds will be found in the quantum theory of the directed valence bond.

D—April 1, 1942.

Varieties of Isomeric Square Complexes.

It is a simple matter to draw up a scheme showing the types of isomeric complexes which are possible on the assumption that Pt^{II} is square coordinated, and it is interesting to see how far these possibilities have been realised in practice. At the same time the scheme will give some idea of the complexity introduced into the chemistry of Pt^{II} by its habit of forming square bonds. All finite mononuclear complexes of quadricovalent Pt^{II} must fall into one or other of these classes :

(*a*) $[PtA_4]^{++}$ (*b*) $[PtA_3X]^{+}$ (*c*) $[PtA_2X_2]^{\circ}$
(*d*) $[PtAX_3]^{-}$ (*e*) $[PtX_4]^{=}$

In the scheme adopted the following symbols have been used :

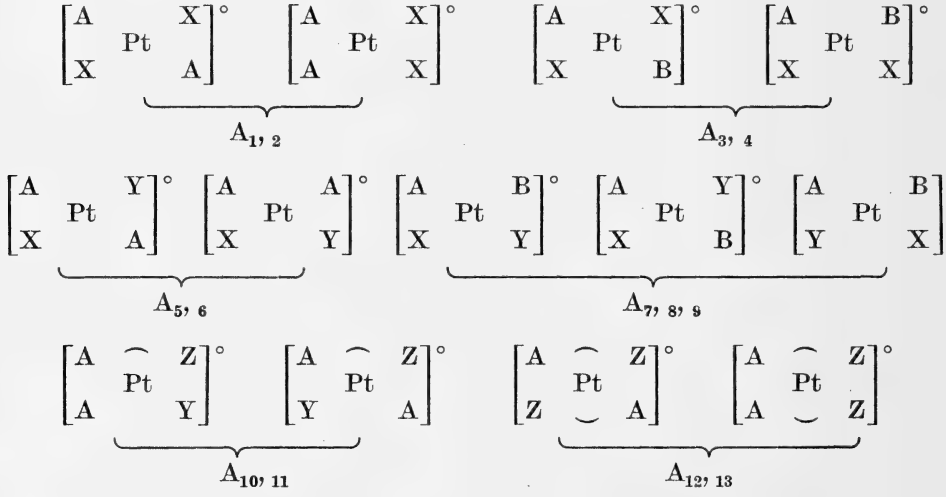
(1) A, B, C, etc., to represent neutral molecules, e.g. NH_3, C_5H_5N, NH_2OH, N_2H_4, $MeNH_2$, $EtNH_2$, $AsCl_3$, $P(CH_3)_3$, Et_2S, etc.

(2) A⌒B to represent an unsymmetrical bidentate chelate group attached by two coordinate links, e.g. isobutylenediamine.

(3) A⌒Z to represent an unsymmetrical chelate group attached by a coordination link and one primary link, e.g. glycine.

(4) X, Y, Z . . . etc., to represent a negatively charged atom or group such as Cl^-, CN^-, NO_2^-, OH^-, etc.

Class A. Non-Electrolyte or Uncharged Complexes.



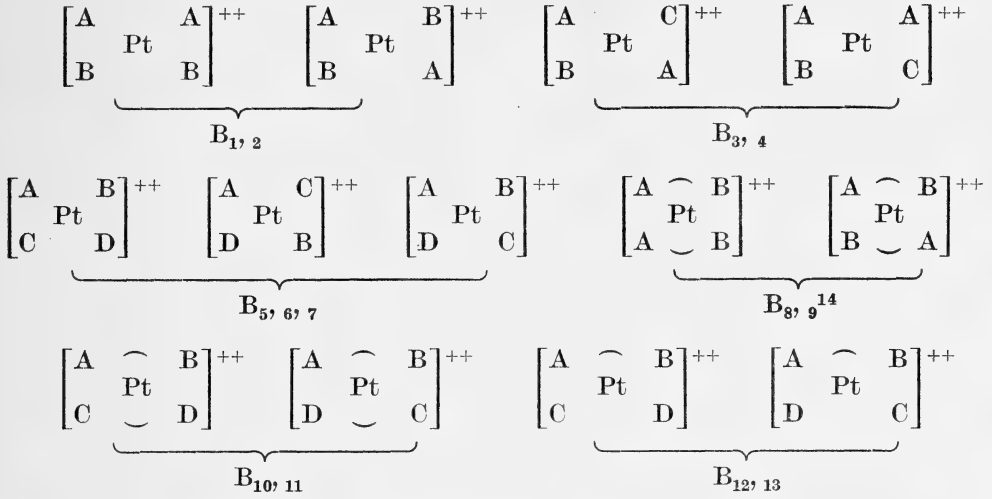
Examples.

$A_{1,2}$: cis and trans $[Pt(NH_3)_2Cl_2]$
$A_{3,4}$: cis and trans $[Pt(NH_3)(Py)Cl_2]$ (Jorgensen, 1866).
$A_{5,6}$: cis and trans $[Pt(NH_3)_2(NO_3)OH]$.
A_7 : $[Pt(C_2H_5)_2S(C_2H_5)_2SeI, Cl]$ (Petren, 1898).
$A_{10,11}$: No examples known.
$A_{12,13}$: $[Pt(NH_2 . CH_2 . COO)_2]$ (Grunberg and Ptizyn, 1933).

Numerous examples of classes $A_{1,2}$ and $B_{1,2}$ have been described throughout the literature. On a rough estimate there must be several hundred examples of isomeric forms of all kinds. The most comprehensive lists are to be found in " A Comprehensive Treatise on Inorganic and Theoretical Chemistry ", Vol. 16, 1937, J. W. Mellor, Longman and Green, London, and in " Handbuch der anorganische Chemie ", Bd. 5, Teil 3, Gmelin and Kraut, Heidelberg. All

allegedly isomeric forms in excess of those required by the hypothesis of square coordination have been shown to be either impure or forms or dimorphs. (Jensen, 1935*b*.)

Class B. Divalent Cationic Complexes.



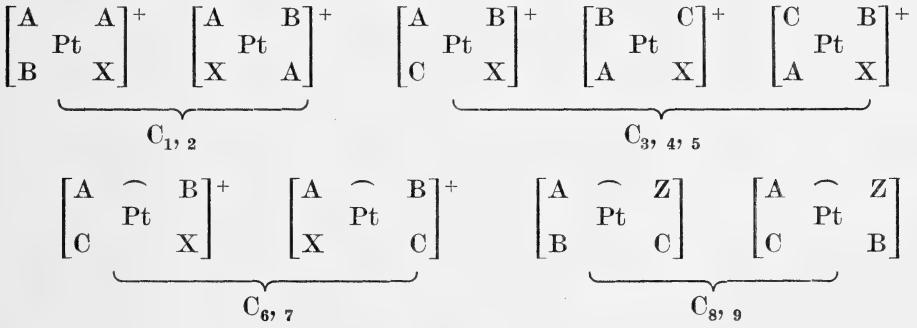
$B_{1,2}$: cis and trans $[Pt(NH_3)_2Py)_2]^{++}$ (Jorgensen, 1866).

$B_{8,9}$: cis and trans $[Pt(NH_2 . C(CH_3)_2 . CH_2NH_2)_2]^{++}$ (Drew and Head, 1934).

$B_{10,11}$: cis and trans $[Pt(NH_2 . CH_2 . CH_2 . C_6H_5 . NH_2)(C_{12}H_{12}N . CH_2NH_2)]^{++}$ (Reihlen, Seipel and Weinbrenner, 1935).

$B_{12,13}$: cis and trans $[Pt(NH_3)(C_2H_5 . NH_2)(NH_2 . C(CH_3)_2 . CH_2NH_2)]^{++}$ (Drew and Head, 1934).

Class C. Monovalent Cationic Complexes.



Examples.

$C_{1,2}$: cis and trans $[Pt(NH_3)_2(NH_2OH)NO_2]^+$ (Tscherniaev, 1926, 1928).

$C_{3,4,5}$: three isomers of $[Pt(NH_3)(Py)(NH_2OH)NO_2]^+$ (Tscherniaev, 1926, 1928). No examples of the other classes are known.

A classification along the same lines could be drawn up for anionic classes of the types : $PtX_2Y_2^=$, $PtX_2YZ^=$. . . . $PtAXYZ^-$, $PtAX_2Y^-$, etc., but as only

[14] Groups other than uni and bidentate have been omitted from this scheme.

one case of isomerism appears to have been recorded among these compounds, and as the classification would simply repeat much of that already given, the scheme will not be pursued further. The discovery of two forms (Riabtchikov, 1940) of

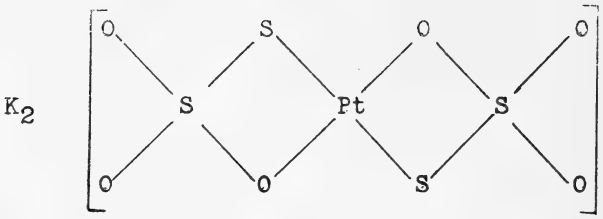
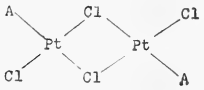


Fig. 21A.

would seem to make it worth while reinvestigating substances like $K_2Pt(NO_2)_2I_2$ (Nilson, 1886) and $K_2Pt(NO_2)_2C_2O_4$ (Vezes, 1903). The scarcity of isomeric forms may well be due to the fact that it is more difficult to make the appropriate substitutions in anionic complexes. No attempt has been made to draw up a scheme for isomeric polynuclear compounds, mainly because no single example of isomerism has yet been found even among those of the simplest type like



(Anderson, 1934), Jensen (1935*b*) and others). More complex polynuclear forms with correspondingly increased possibilities of isomerism are conceivable, but there is practically no evidence for them to date. In this regard certain cyano compounds would probably repay investigation. For example the composition of one of them described long ago by Cleve (1872), namely $[PtNH_3(CN)_2]_x$, suggests that it may have the structure

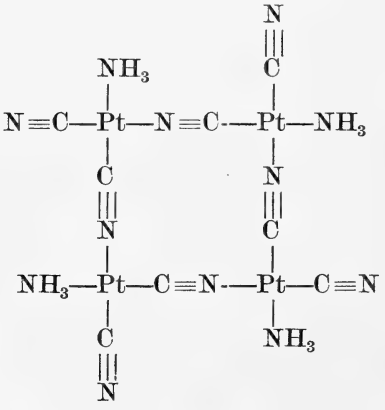


Fig. 21B.

Theoretical Evidence.

By the application of general quantum mechanical principles to the problem of the orientation of chemical bonds Pauling (1931) has, on the basis of a single

postulate,[15] derived a large number of results of great stereochemical interest. It is perhaps no serious test of the theory of the directed bond that it predicts the square bonding of Pt^{II}, although the general evidence for this latter was not so strong at that time (1931). Nor should it be implied that support for the quantum mechanical theory of the directed bond comes only from the experimental results dealing with quadricovalent elements. It is, however, necessary to restrict the discussion here to the deductions of the theory relating to such elements. The relevant rules are these :

(1) Square bonds will be formed whenever dsp^2 orbitals are involved in bond formation.
(2) Tetrahedral bonds will be formed whenever sp^3 orbitals are involved in bond formation.

Any atom whose structure is such as will permit the use of dsp^2 orbitals, that is any atom with a vacant d orbital just within its valence shell, will form square, rather than tetrahedral bonds, because by so doing a more stable structure will result. The electronic structure of Pt^{II} fulfils just these conditions.

From the numerous examples of planar structure already dealt with, and from the above rule, it is a fair inference to conclude that square bonding is as universal among platinous compounds as tetrahedral bonding is among carbon compounds.

Non-Planar Structures.

Such an inference does, however, require several qualifications.

Firstly the above bonding rules refer only to electron pair or covalent bonds. If the difference between the electronegativities of the atoms is sufficiently large they may be held together by predominantly ionic tetrahedral bonds which do not involve pairing of electrons as in covalent bond formation. The mere fact of an atom forming square bonds shows that the bonds are covalent, since the configuration of minimum potential energy for four ionic bonds is the tetrahedral one. As will be discussed more fully in the sequel, the magnetic criterion may be used to distinguish between the two bond types. If Pt^{II} formed ionic bonds, i.e. if platinum existed as the Pt^{++} ion in any of its compounds, these should be paramagnetic with susceptibilities corresponding to the presence of two unpaired electron spins. As a matter of actual experience all platinous compounds examined to date have proved to be diamagnetic, from which we can infer that platinum does not exist in the ionic condition in any of these compounds. About the only likely compounds in which Pt^{++} might be found are those with fluorine, the most electronegative of all elements, but very little is known of such compounds. The few referred to in the literature (Mellor, J. W., 1937) are by no means well defined, and in no case has any magnetic work been done on them. Nevertheless this possible exception to the general rule must be borne in mind.

Secondly the bonding rules refer only to compounds in which Pt^{II} has a coordination number four. While this number seems almost universal, there are one or two rare but well authenticated cases where it rises to six. So far the proofs are chemical, and some useful work remains to be done in checking the chemical findings by crystal structure analyses or by some other means. There are at least two compounds in which the chemical evidence for a coordina-

[15] " Of two orbitals in an atom the one which can overlap more with an orbital of another atom will form the stronger bond with that atom and moreover, the bond formed by a given orbital will tend to be in that direction in which the orbital is concentrated " (Pauling, 1939).

Another way of putting this is to say that " the bond energy is lowest and the bond consequently most stable, if there is as much overlapping as possible between the wave function or orbital of a given electron and that of the electron with which it is paired and as little as possible between it and those of all other electrons on other atoms " (Rice, 1940).

tion number six is strong: the platinous bis αβγ-triaminopropane complex (Mann and Pope, 1926*a*; Mann, 1929) and cis and trans bisacetonitrile tetrammine platinous chloride (Tschugaeff, 1915). There may be other instances, but they are rare and certainly do not include substances like $[Pt(NH_3)_4]Cl_2$, to which Hantzsch and Rosenblatt (1930) have attributed an octahedral structure. Crystal structure evidence on this last substance is quite definitely against octahedral coordination.

Finally, it must be emphasised that the quantum mechanical rules relating to the directed chemical bond refer only to bonds *free to arrange* and that where this condition obtains the bond angles found are very close to those required by theory. Thus electron diffraction studies show that in methylene chloride, chloroform, propane, isobutane and other such molecules the angles between single bonds to carbon are from 109° to 112°, close to the tetrahedral value of 109° 28′. Yet there is not the slightest doubt that in cyclopropane the angles between single bonds to carbon are 60°. Permanent bond angle distortions inherent in the configuration adopted by a molecule are by no means rare (Mellor, 1940) and must be allowed for in discussing the stereochemistry of platinum. Crystal structure analyses reveal bond angles of 90° in K_2PtCl_4, $Pt(NH_3)_4Cl_2$, etc., but there may well arise instances where, under duress, as it were, such large bond angle distortions may be produced as to alter completely the symmetry of a complex. Two examples of what may be called "forced configurations" will be considered here. The first is the compound ββ′β″ triaminotriethylamine platinous chloride described by Mann and Pope (1926*b*). If platinum is regarded as having a coordination number four, then it is sterically impossible for it to be square coordinated here. (See Fig. 22.)

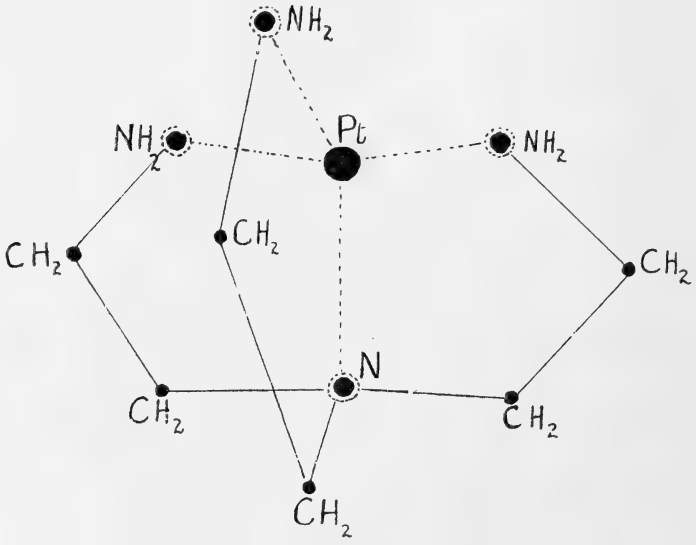


Fig. 22.

Platinum might conceivably be octahedrally coordinated in this compound but without a crystal analysis it is difficult to eliminate this possibility with any degree of certainty. The same objection does not apply to compounds containing bis - 3 : 3′ : 5 : 5′ - tetramethyl - 4 : 4′ - dicarbethoxydipyrromethene (Fig. 23A).

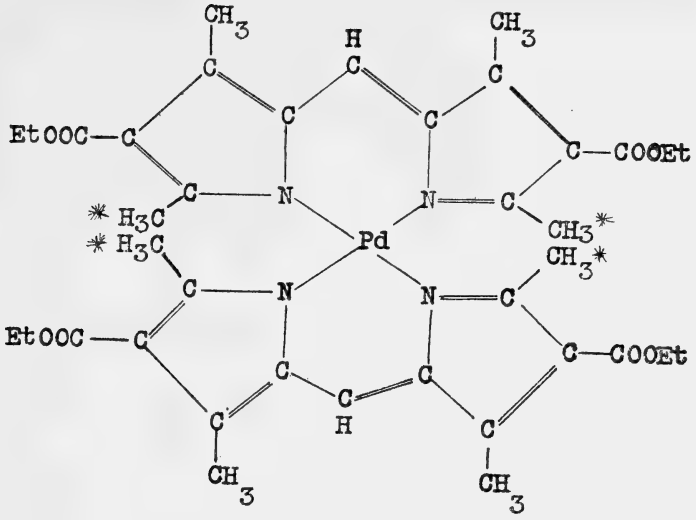


Fig. 23A.

Porter has shown that if this substituted pyrromethene, with methyl groups in the α positions, functions as a bidentate chelate group, and the evidence is that with many metals it does, then any attempt on the part of the chelate to assume a planar configuration is prevented by steric hindrance. The α methyl groups (asterisked in Fig. 23A) must clash. The clashing is more serious than might be gathered from Fig. 23A. In redrawing it with the appropriate dimensions (Fig. 23B) the extent of the overlapping of the methyl groups is indicated by horizontal shading. It should be pointed out that, owing to resonance in the pyrrole ring, the α methyl groups and the ring would normally be coplanar.

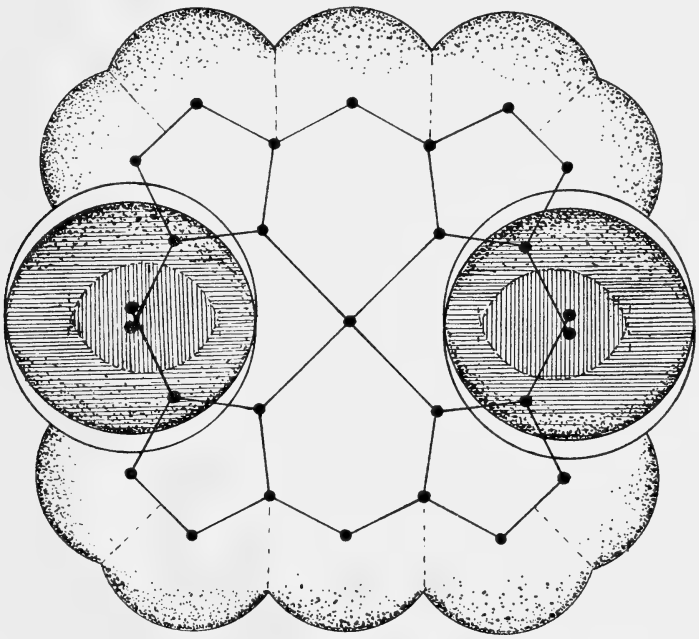


Fig. 23B.

Under stress the methyl groups might be bent to some small extent out of the plane of the pyrrole ring, but because of the large van der Waal's radius of the methyl group, 2 A.U., no amount of distortion of the C-CH_3 could accommodate chelating dipyrromethene groups in square coordinated positions. By assuming that the methyl groups remain in the plane of the pyrrole rings, and that all the distortion occurs in the Me-N bonds, a rough calculation shows that the distortion amounts to about 40° (Mellor and Craig, 1940*a*).

Although quite a number of metal derivatives of this di-pyrromethene have been described, curiously enough the platinum derivative does not appear among them. However the palladium compound has been prepared (Porter, 1938 ; Mellor and Lockwood, 1940), and there is little doubt that platinum can also form a compound.

Incidence of the Square Configuration among other Metallic Complexes.

The metals for which square coordination is theoretically possible are those whose electronic structures permit the use of dsp^2 orbitals in bond formation, that is to say, those which have a vacant *d* orbital within the valence shell. The elements which fulfil this condition are confined to the three transition series of the periodic table. Table 4, drawn up primarily (Pauling and Huggins, 1934) to show the magnetic moments predicted for the transition elements in different stereochemical configurations, will be used as a basis for discussion.

Table 4.

Predicted Magnetic Moments of Complexes Containing Transition Elements.

	The Iron Group.	The Palladium Group.	The Platinum Group.	No. of electrons in d shell (3d, 4d or 5d).	For ionic or sp^3 (tetrahedral) bonds.	For 4 dsp^2 (square) bonds.	For 6 d^2sp^3 (octahedral) bonds.
1	$K^{I}Ca^{II}Sc^{III}Ti^{IV}$	$Rb^{I}Sr^{II}Y^{III}Qr^{IV}Nb^{V}Mo^{VI}$	$Cs^{I}Ba^{II}$–$Hf^{IV}Ta^{V}W^{VI}$	0	0·00	0·00	0·00
2	V^{IV}	$Nb^{IV}Mo^{V}$	W^{V}	1	1·73	1·73	1·73
3	$V^{III}Cr^{IV}$	$Mo^{IV}Ru^{VI}$	$W^{IV}Os^{VI}$	2	2·83	2·83	2·83
4	$V^{II}Cr^{III}Mn^{IV}$	Mo^{III}		3	3·88	3·88	3·88
5	$Cr^{II}Mn^{III}Fe^{IV}$	$Mo^{II}Ru^{IV}$	Os^{IV}	4	4·9	4·9	2·83
6	$Mn^{II}Fe^{III}Co^{IV}$	Ru^{III}	$Os^{III}Ir^{IV}$	5	5·91	3·88	1·73
7	$Fe^{II}Co^{III}$	$Ru^{II}Rh^{III}Pd^{IV}$	$Ir^{III}Pt^{IV}$	6	4·90	2·83	0·00
8	$Co^{II}Ni^{III}$	Rh^{II}		7	3·88	1·73	
9	Ni^{II}	$Rh^{I}Pd^{II}Ag^{III}$	$Pt^{II}Au^{III}$	8	2·83	0·00	
10	Cu^{II}	Ag^{II}		9	1·73		
11	$Cu^{I}Zr^{II}Ge^{IV}$	$Ag^{I}Cd^{II}In^{III}$	$Au^{I}Hg^{II}Ti^{III}Pb^{IV}B^{V}$	10	0·00		

This table is taken (modified) from the paper by L. Pauling and M. L. Huggins, *Zeit. für Krist.*, **87**, 1934, 214.

It should be explained that the magnetic dipole moment of an atom arises from the existence in it of unpaired electron spins : the magnitude of the moment, in Bohr magnetons, the units employed in the table, is given by the expression $\mu = \sqrt{n(n+2)}$, where n is the number of unpaired spins. For diamagnetic substances n=0.

Several interesting features of Table 4 call for comment. In the first place it will be seen that the magnetic distinction between ionic, tetrahedral, and square coordination can be made only with elements in horizontal rows 6, 7, 8 and 9. Secondly, although square coordination is theoretically possible with any element of the three transition series it has actually been found with very few (shown in heavy type), and these are confined to the relatively small portion

of the table marked off with a heavy line. It is significant that the square structure is most common among elements with 0 or 1 unpaired electrons (Pt^{II}, Pd^{II}, Au^{III}, Ni^{II}, Co^{II}, Cu^{II}, Ag^{II}), very rare or doubtful among those with 2 or 3 (Fe^{II}, Mn^{II}), and as far as is known non-existent among those with the maximum number possible, four. The numbers of unpaired electrons just quoted refer of course to the different atoms in the square coordinated condition. The same tendency to assume configurations with small numbers of unpaired electrons is to be seen among the diamagnetic complexes of Co^{III}, Pt^{IV}[16] Pd^{IV}, and Ir^{IV}, which are invariably octahedral. These observations may be summarised in a general rule which states that, when a metal atom of the transition series forms a covalent complex, it tends to assume that configuration (tetrahedral, square, octahedral, etc.) which involves the least possible number of unpaired electrons.

The usefulness of a theory is determined largely by the extent to which its predictions check satisfactorily with experiment. In this respect the quantum theory of the directed valence bond has fared well. For example, it predicted (Pauling, 1931)[17] that the diamagnetic complexes of Ni^{II} and Au^{III} would have the square structure ; in both instances crystal analyses and other investigations have amply borne this out.

Where definite evidence for square coordination has been found for any element it may be assumed that it will be found in this condition generally, unless (1) the element is octahedrally coordinated, (2) steric effects cause bond angle distortion, (3) marked electronegativity differences produce predominantly ionic (tetrahedral) binding. It is true that some elements, notably Fe^{II} and Mn^{II}, are so very sensitive to this last factor that they are seldom square coordinated. On the other hand the above provisos rarely have to be invoked for Pt^{II}, Pd^{II}, Cu^{II} and Au^{III}.

Square Complex Formation with Metals other than Platinum.

Palladium.

This element resembles platinum very closely except in one respect. Neither the geometrical nor the optical isomers of Pd^{II} retain their configurations with the same tenacity as those of Pt^{II}. Geometrical isomerism is confined, so far as the observations go, to neutral complexes. In summarising the evidence for this and the metals to follow, the nature of the investigation will first be indicated and then the compound in which the square structure has been found.

Crystal Structure.—K_2PdCl_4 (Dickinson, 1922 ; Theilacker, 1937), PdO (Lunde, 1927), $[Pd(NH_3)_4]Cl_2$ (Dickinson, 1934), $K_2[Pd(COS)_4]$ (Cox, Wardlaw and Webster, 1935*d*), $(Me_2S)PdCl_2$ (Cox, Saenger and Wardlaw, 1934), PdS (Gaskell, 1937), $PdCl_2$ (Wells, 1938), $(Me_3As)_2Pd_2Br_2$ (Mann and Wells, 1938), $[(NH_3)_2PdC_2O_4]$ (Mann, Crowfoot, Gattiker and Wooster, 1935*b*).

Geometrical Isomerism.—Cis and trans forms of benzylmethylglyoxime palladium (Dwyer and Mellor, 1935), cis and trans bis-glycine-palladium (Pinkard, Sharratt and Wardlaw and Cox, 1934), cis and trans dichlorodiammine palladium (Grunberg and Schulman, 1933), cis and trans $[(NH_3)_2Pd(NO_2)_2]$ (Mann *et al.*, 1935*b*).

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[16] If the results of the incomplete X-ray study (Cox and Webster, 1935*a*) of $Pt(CH_3)_3Cl$ are correct, this compound should have a magnetic moment of 4·9 Bohr magnetons, which, in view of the data so far available for platinum compounds, is very unlikely. Platinum is most likely octahedrally coordinated in this compound as in $Pt(CH_3)_4$ (Pauling, 1940).

[17] At the time this prediction was made the observation that bis methylgloxime nickel exists in two forms (Tschugaeff, 1910) which might reasonably be cis-trans planar isomerides appears to have been overlooked. In any case, magnetic susceptibilities of nickel glyoxime complexes were not investigated until 1932 (Sugden), when further instances of isomerism were brought to light.

Optical Isomerism.—Isobutylenediaminestilbenediamine palladous salts (Lidstone and Mills, 1939).

Dipole Moments.—$PdCl_2(AsR_3)_2$ (Mann and Purdie, 1935*a*), $PdCl_2(Et_3Sb)_2$ (Jensen, 1936*a*).

Crystal Optics.—K_2PdCl_4 (Mellor and Quodling, 1935), $BaPd(CN)_4 4H_2O$, etc. (Brasseur and de Rassenfosse, 1937).

Magnetic Susceptibilities.—K_2PdCl_4, etc. (Janes, 1935).

Nickel.

This is the first element so far considered for which there is evidence of both the square and tetrahedral configuration, although it must be admitted that the evidence for the latter is as yet rather meagre. Except in one instance, geometrical isomerism is confined to internal complexes and is not specially common even here. From some preliminary work on the factors which determine whether nickel shall be square or tetrahedrally coordinated it would seem that electronegative differences between nickel and the atoms linked to it play a major role (Mellor and Craig, 1940). There is also evidence that extensive deflection of bond directions, which, in the absence of steric influences would be expected to assume the square orientation, results in a marked change bond character (Mellor and Lockwood, 1940).

Paramagnetic and diamagnetic nickel compounds lend themselves to studies on correlations between bond character and absorption spectra and one or two interesting results in this connection have already been reported (Mills and Mellor, 1942). A notable characteristic of diamagnetic nickel compounds is their marked resistance to assuming sixfold coordination. Paramagnetic nickel complexes with a coordination number four, on the other hand, quite readily take up two additional groups to assume the octahedral configuration (Dwyer and Mellor, 1941).

It is very interesting to note a similar kind of behaviour in ionic Fe^{II} complexes with coordination number four (ferrohemoglobin, etc.), where the change to a diamagnetic octahedral covalent Fe^{II} complex can be readily brought about. The metals which easily form square bonds could not well play the same role as Fe^{II} in the blood pigments.

Crystal Structure.—$K_2[Ni(COS)_4]$ (Cox, Wardlaw and Webster, 1935*d*; Elliott, 1938), $Ba[Ni(CN)_4]4H_2O$ (Brasseur and de Rassenfosse, 1938), $Na_2[Ni(CN)_4]3H_2O$ (Brasseur and de Rassenfosse, 1941), bis N-N′-dipropyldithiocarbamate-nickel (Peyronel, 1941).

Geometrical Isomerism.—Bis-methylglyoxime nickel (Tschugaeff, 1910), bis benzylmethylglyoxime (Sugden, 1932), bis thiosemicarbazide nickelous sulphate (Jensen, 1936*b*).

Dipole Moments.—$[NiBr_2(Et_3P)_2]$ ($\mu=0$) and related compounds (Jensen, 1936*a*), nickel glyoximes (Cavell and Sugden, 1935).

Crystal Optics.—$K_2[Ni(CN)_4]$ (Mellor and Quodling, 1936), $Ba[Ni(CN)_4$, etc. (Brasseur and de Rassenfosse, 1937).

Magnetic Susceptibilities.—Nickel ethyldithiocarbonate, etc. (Cambi and Szego, 1931), a wide range of nickel complexes (Mellor and Craig, 1940), bis-phenylethylenediamine nickel chloride, etc. (Lifschitz, Bos and Dijkema, 1939).

All the compounds mentioned in the above summary are diamagnetic.

Evidence relating to tetrahedral paramagnetic nickel compounds has been discussed in this Journal (Mellor, 1941).

Gold (Au^{III}).

In the trivalent condition gold undoubtedly forms square bonds, but it is extremely doubtful whether it does so in the monovalent condition. Further

work substantiating the claims of Dothie, Llewellyn, Wardlaw, and Welch (1939) is needed before it can be accepted that Au^{I} can be grouped with Au^{III}.

It is noteworthy that no geometrically isomeric auric compounds have been observed in spite of the definite searches made for them.

Crystal Structure.—$K[AuBr_4]2H_2O$ (Cox and Webster, 1936*c*), $[(AlK)_2AuBr_2]_2$ etc. (Burawoy, Gibson, Hampson and Powell, 1937), $[Pr_2AuCN]_4$ (Powell and Phillips, 1938), $Cs_2Au_2Cl_6$ (Elliott and Pauling, 1938), $[N(C_2H_5)_4]AuCl_4$ (Huggins, unpublished data).

Crystal Optics.—$[N(C_2H_5)_4]AuCl_4$, $K[AuBr_4]2H_2O$ (Mellor *et al.*, 1936).

Silver (Ag^{II}).

The only instance so far described is argentic picolinate. An incomplete X-ray analysis of this substance made by Cox, Wardlaw, and Webster (1936*b*) shows the presence of square complexes.

Copper (Cu^{II}).

An outstanding characteristic of copper is that it is much less sensitive to electronegative differences (from a stereochemical viewpoint) than its close neighbours like Ni^{II}, Co^{II}. Several hydrated salts of copper are known, from crystal analyses, to form square complexes, e.g. $CuCl_2 2H_2O$, $K_2CuCl_4 2H_2O$ and $CuSO_4 5H_2O$. No diamagnetic hydrated nickel chloride or sulphate has been reported.

It is very doubtful whether any tetrahedral cupric complexes have yet been found. Arguing by analogy Mills and Gotts (1926) concluded that cupribenzoylpyruvic acid had a tetrahedral structure. It is practically certain that the analogy does not hold.

Large numbers of internal copper complexes containing unsymmetrical chelate groups have been described throughout the literature, and it is extraordinary that so few geometrical isomers have been discovered. One can only conclude that cis isomers must be so unstable as to be incapable of existing for any length of time.

Crystal Structure.—$CuCl_2 2H_2O$ (Harker, 1936), $K_2CuCl_4 2H_2O$ (Chrobak, 1934), copper diketones (Cox and Webster, 1935*b*), $CuSO_4 5H_2O$ (Beevers and Lipson, 1934), CuO (Tunnel, Posnjak and Ksanda, 1935), $CuPy_2Cl_2$ (Cox, Sharatt, Wardlaw and Webster, 1936*a*).

Geometrical Isomerism.—$[Cu_2Cl_3(Ph_2Me)_3As)_3]$ (Mellor, Burrows and Morris, 1938*a*), cupric polymethylene bis-imino-acid complexes (Schlesinger, 1925), cupric picolinate (Cox, Wardlaw and Webster, 1936*b*).

Cobalt (Co^{II}).

The only evidence to date comes from magnetic susceptibility measurements which show that certain internal complexes have a moment corresponding to the existence of one unpaired electron, the number to be expected for a square structure. Magnetic data show that α and β $CoPy_2Cl_2$ are not square forms.

Magnetic Susceptibilities.—Bis-benzildioxime cobalt (Cambi and Malatesta, 1939), many other internal complexes (Mellor and Craig, 1940*b*), $CoPy_2Cl_2$ (Barkworth and Sugden, 1937 ; Mellor and Coryell, 1938*b*).

Rhodium (Rh^{II}).

All attempts to prepare square rhodous complexes with one unpaired electron spin have so far resulted in failure.[18]

[18] Unpublished experiments with F. P. Dwyer.

Iron (Fe^{II}) and Manganese (Mn^{II}).

Many compounds have been examined[19] in the hope of finding evidence for the square configuration, but without success. Such compounds appear to be very rare and the only ones reported to date are ferrous and manganous phthalocyanine (Senff and Klemm, 1939). Several years ago, Cox, Shorter, Wardlaw, and Way (1937), on the basis of a determination of unit cell dimensions, reported that manganous dipyridine chloride $[MnPy_2Cl_2]$ had the trans square structure. This was subsequently shown to conflict with the magnetic data, which indicated that manganese in this compound was definitely in the ionic condition (Mellor and Coryell, 1938*b*). An alternative octahedral structure was suggested as a way of explaining the small cell dimensions. The structure attributed to the $[Mn(H_2O)_4]^{++}$ ion in $K_2Mn(SO_4)_24H_2O$ (Anspach, 1939) is almost certainly incorrect.

Iridium (Ir^{I}).

As already pointed out, the higher valence states of iridium, platinum, etc., are invariably octahedrally coordinated. It is only in its lowest valency state, in a compound like IrCl for example, that iridium is likely to have the square structure. So far no results have been reported for compounds of this metal.

Before concluding this brief survey, some reference must be made to a number of claims regarding the square configuration for metals not listed in Table 4 as capable of forming dsp^2 bonds. The evidence for square Tl^{I} and Au^{I} rests mainly on a small unit of dimension for certain of their compounds (Cox, Shorter and Wardlaw, 1938; Dothie *et al.*, 1939) and cannot be regarded as satisfactory. With regard to earlier claims relating to the structure of Cd^{II} (Brasseur and de Rassenfosse, 1936), Pb^{II} and Sn^{II} (Cox, Shorter and Wardlaw, 1937*b*), all that need be stated here is that subsequent investigation has shown that octahedral coordination prevails (Brasseur and de Rassenfosse, 1939; MacGillavray, De Wilde and Bijvoet, 1938) in these compounds.

Summary.

Traditional chemical methods of unravelling questions of molecular structure fail to provide a unique solution to the problem of the structure of bivalent platinum compounds. The various alternative interpretations of the phenomena of geometrical and mirror image isomerism can be narrowed down by spectroscopic and dipole moment measurements but the final solution is provided by the results of crystal structure analysis. The great mass of data on platinum together with that just listed for other metals leaves no reasonable doubt that certain elements can form square bonds. With the reservation that it applies only to bonds free to arrange, the theory of the directed valence bond makes it clear just what metal atoms are likely to form square bonds and at the same time it provides certain criteria for deciding whether any given atom has adopted that configuration. While the purely stereochemical problem of the existence of square complexes can be considered as settled, much remains to be done on problems relating to their general chemical behaviour.

References.

Anderson, J. S., 1934. *J. Chem. Soc.*, 971.
Angell, F. G., Drew, H. D. K., and Wardlaw, W., 1930. *J. Chem. Soc.*, 349.
Anspach, H., 1939. *Z. Krist.*, **101**, 39.
Babayeva, A. A., 1938. *C.R. Acad. Sc. U.R.S.S.*, **20**, 365.
Bannister, F. H., and Hey, M. H., 1932. *Min. Mag.*, **23**, 188.
Barkworth, E. D. P., and Sugden, S., 1937. *Nature*, **139**, 374.
Beevers, C. A., and Lipson, H., 1934. *Proc. Roy. Soc. A.*, **146**, 570.

[19] Unpublished work with D. P. Craig.

Born, M., 1923. Atomtheorie des Festen Zustandes. Teubner, Leipzig.
Bragg, W. L., 1924. *Proc. Roy. Soc. A.*, **105**, 370.
Brasseur, H., and de Rassenfosse, A., 1936. *Z. Krist.*, **95**, 474.
Brasseur, H., and de Rassenfosse, A., 1937. *Mem. Acad. roy. Belg.*, **16**, 1.
Brasseur, H., and de Rassenfosse, A., 1938. *Bull. Soc. Fr. Min.*, **61**, 129.
Brasseur, H., and de Rassenfosse, A., 1939. *Z. Krist.*, **101**, 389.
Brasseur, H., and de Rassenfosse, A., 1941. *Mem. Acad. roy. Belg.*, [2], **4**, 397.
Burawoy, A., Gibson, C. S., Hampson, G. C., and Powell, H. M., 1937. *J. Chem. Soc.*, 1690.
Cambi, L., and Malatesta, L., 1939. *Gazz. Chim. Ital.*, **69**, 547.
Cambi, L., and Szego, L., 1931. *Ber. dtsch. Gess. Chem.*, **64**, 2591.
Cavell, H. J., and Sugden, S., 1935. *J. Chem. Soc.*, 621.
Chrobak, L., 1934. *Z. Krist.*, **88**, 35.
Cleve, P. T., 1872. *Kong. Svenska Vetens Akad. Handl.*, **9**, 1.
Cossa, A., 1890. *Ber. dtsch. Chem. Gess.*, **23**, 2504.
Cox, E. G., 1932. *J. Chem. Soc.*, 1912.
Cox, E. G., and Preston, G. H., 1933. *J. Chem. Soc.*, 1089.
Cox, E. G., Saenger, H., and Wardlaw, W., 1934*a*. *J. Chem. Soc.*, 182.
Cox, E. G., and Webster, K. C., 1935*a*. *Z. Krist.*, **90**, 561.
Cox, E. G., and Webster, K. C., 1935*b*. *J. Chem. Soc.*, 731.
Cox, E. G., Pinkard, F. W., Wardlaw, W., and Webster, K. C., 1935*c*. *J. Chem. Soc.*, 459.
Cox, E. G., Wardlaw, W., and Webster, K. C., 1935*d*. *J. Chem. Soc.*, 1475.
Cox, E. G., Sharrat, E., Wardlaw, W., and Webster, K. C., 1936*a*. *J. Chem. Soc.*, 129.
Cox, E. G., Wardlaw, W., and Webster, K. C., 1936*b*. *J. Chem. Soc.*, 775.
Cox, E. G., and Webster, K. C., 1936*c*. *J. Chem. Soc.*, 1635.
Cox, E. G., Shorter, A. J., Wardlaw, W., and Way, W. J. R., 1937*a*. *J. Chem. Soc.*, 1556.
Cox, E. G., Shorter, A. J., and Wardlaw, W., 1937*b*. *Nature*, **139**, 71.
Cox, E. G., Shorter, A. J., and Wardlaw, W., 1938. *J. Chem. Soc.*, 1886.
Dickinson, R. G., 1922. *J. Amer. Chem. Soc.*, **44**, 2404.
Dickinson, B. N., 1934. *Z. Krist.*, **88**, 281.
Dothie, H. J., Llewellyn, F. J., Wardlaw, W., and Welch, A. J. E., 1939. *J. Chem. Soc.*, 426.
Drew, H. D. K., 1932. *J. Chem. Soc.*, 2328.
Drew, H. D. K., Pinkard, F. W., Wardlaw, W., and Cox, E. G., 1932*a*. *J. Chem. Soc.*, 988.
Drew, H. D. K., Pinkard, F. W., Wardlaw, W., and Cox, E. G., 1932*b*. *J. Chem. Soc.*, 1004.
Drew, H. D. K., and Head, F. S. H., 1934. *J. Chem. Soc.*, 221.
Dwyer, F. P., and Mellor, D. P., 1934. *J. Amer. Chem. Soc.*, **56**, 1551.
Dwyer, F. P., and Mellor, D. P., 1935. *J. Amer. Chem. Soc.*, **63**, 1392.
Dwyer, F. P., and Mellor, D. P., 1941. *J. Amer. Chem. Soc.*, **63**, 81.
Elliott, N., and Pauling, L., 1938. *J. Amer. Chem. Soc.*, **60**, 1846.
Elliott, N., 1938. Dissertation. *Calif. Inst. Technology*, Pasadena.
Fritzmann, E., 1912. *Z. anorg. Chem.*, **73**, 239.
Gaskell, T. F., 1937. *Z. Krist.*, **96**, 203.
Gelman, A. D., and Bauman, M., 1938. *C.R. Acad. Sc. U.R.S.S.*, **18**, 645.
Grailich, J., 1858. *S.B. Akad. Wiss, Wien*, **32**, 50.
Grunberg, A. A., 1926. *Z. anorg. Chem.*, **157**, 299.
Grunberg, A. A., 1931. *Helv. Chim. Act.*, **14**, 455.
Grunberg, A. A., and Ptizyn, B. W., 1933*a*. *J. prakt. Chem.*, **136**, 143.
Grunberg, A. A., and Schulman, V. M., 1933*b*. *C.R. Acad. Sc., U.R.S.S.*, 218.
Hantzsch, A., and Rosenblatt, F., 1930. *Z. anorg. Chem.*, **187**, 24.
Hantzsch, A., 1926. *Ber. dtsch. Gess. Chem.*, **59**, 2761.
Harker, D., 1936. *Z. Krist.*, **93**, 136.
Helmholtz, L., 1936. *J. Chem. Phys.*, **4**, 316.
Hibben, J. H., 1939. The Raman Effect, Reinhold, New York.
Hylleraas, E., 1927. *Z. Krist.*, **65**, 469.
Janes, R. B., 1935. *J. Amer. Chem.*, **57**, 471.
Jensen, K. A., 1935*a*. *Z. anorg. Chem.*, **225**, 97.
Jensen, K. A., 1935*b*. *Z. anorg. Chem.*, **225**, 115.
Jensen, K. A., 1936*a*. *Z. anorg. Chem.*, **229**, 225.
Jensen, K. A., 1936*b*. *Z. anorg. Chem.*, **229**, 265.
Jensen, K. A., 1938. *Z. anorg. Chem.*, **241**, 115.
Jorgensen, S. M., 1886. *J. prakt. Chem.*, **33**, 489.
King, H. J. S., 1938. *J. Chem. Soc.*, 1938.
Kurnakow, J., 1894. *J. prakt. Chem.*, **50**, 483.
Lidstone, A. G., and Mills, W. H., 1939. *J. Chem. Soc.*, 1754.
Lifschitz, I., Bos, J. G., and Dijkema, K. M., 1939. *Z. anorg. Chem.*, **242**, 97.
Lunde, G., 1927. *Z. anorg. Chem.*, **163**, 345.
Magnus, G., 1828. *Poggendorff's Ann.*, **14**, 239.
MacGillavry, C. H., de Wilde, J. H., and Bijvoets, J., 1938. *Z. Krist.*, **100**, 212.
Mann, F. G., and Pope, W. J., 1926*a*. *J. Chem. Soc.*, 482.
Mann, F. G., and Pope, W. J., 1926*b*. *J. Chem. Soc.*, 2675.

Mann, F. G., 1929. *J. Chem. Soc.*, 651.
Mann, F. G., and Purdie, D., 1935*a*. *J. Chem. Soc.*, 1549.
Mann, F. G., Crowfoot, D., Gattiker, D., and Wooster, N., 1935*b*. *J. Chem. Soc.*, **1642**.
Mann, F. G., and Wells, A. F., 1938. *J. Chem. Soc.*, 702.
Mathieu, J. P., 1939. *J. Chim. Phys.*, **36**, 271, 308.
Mellor, D. P., and Quodling, F. M., 1935. This Journal, **69**, 167.
Mellor, D. P., and Quodling, F. M., 1936. This Journal, **70**, 205.
Mellor, D. P., and Morris, B. S., 1938. This Journal, **71**, 536.
Mellor, D. P., Burrows, G. J., and Morris, B. S., 1938*a*. *Nature*, **141**, 414.
Mellor, D. P., 1940. This Journal, **74**, 129.
Mellor, D. P., and Lockwood, W. H., 1940. This Journal, **74**, 141.
Mellor, D. P., and Craig, D. P., 1940*a*. This Journal, **74**, 495.
Mellor, D. P., and Craig, D. P., 1940*b*. This Journal, **74**, 475.
Mellor, D. P., and Coryell, C. D., 1938*b*. *J. Amer. Chem. Soc.*, **60**, 1786.
Mellor, J. W., 1937. A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 16. Longman, London.
Mills, J. E., and Mellor, D. P., 1942. *J. Amer. Chem. Soc.*, **64**, 181.
Mills, W. H., and Quibell, T. H. H., 1935. *J. Chem. Soc.*, 839.
Mills, W. H., and Gotts, R. A., 1926. *J. Chem. Soc.*, 3121.
Moore, W. J., and Pauling, L., 1941. *J. Amer. Chem. Soc.*, **63**, 1392.
Morgan, G. T., and Burstall, F. H., 1934. *J. Chem. Soc.*, 965.
Nilson, J., 1886. *J. prakt. Chem.*, **21**, 179.
Ostromisslensky, I., and Bergmann, A., 1910. *Ber. dtsch. Chem. Gess.*, **43**, 2768.
Pauling, L., 1931. *J. Amer. Chem. Soc.*, **53**, 1367 ; 1932. *Ibid.*, **45**, 994.
Pauling, L., and Huggins, M., 1934. *Z. Krist.*, **87**, 214.
Pauling, L., 1939. The Nature of the Chemical Bond. Cornell Univ. Press, New York, 1st ed., 81.
Pauling, L., 1940. The Nature of the Chemical Bond. Cornell Univ. Press, New York, 2nd ed., 102.
Peyrone, M., 1844. *Ann. Chim. Phys.*, **12**, 93.
Peyrone, M., 1846. *Ann. Chim. Phys.*, **16**, 462.
Peyrone, M., 1845. *C.R. Acad. Sci. Paris*, **18**, 1103.
Peyronel, G., 1941. *Z. Krist.*, **103**, 57.
Petren, I., 1898. Dissertation Lund. 1910, *Z. anorg. Chem.*, **20**, 62.
Pinkard, F. W., Saenger, H., and Wardlaw, W., 1933. *J. Chem. Soc.*, 1056.
Pinkard, F. W., Sharrat, E., Wardlaw, W., and Cox, E. G., 1934. *J. Chem. Soc.*, 1012.
Porter, C. R., 1938. *J. Chem. Soc.*, 368.
Powell, H., and Phillips, R. F., 1938. Br. Assn. Adv. Sc., 50.
Reihlen, H., and Nestle, K., 1926. *Liebig's Ann.*, **447**, 211.
Reihlen, H., and Huhn, W., 1931. *Leibig's Ann.*, **489**, 42.
Reihlen, H., Seipel, G., and Weinbrenner, E., 1935. *Leibig's Ann.*, **520**, 256.
Reiset, J., 1844. *C.R. Acad. Sc. Paris*, **18**, 1103.
Riabtchikov, D. I., 1940. *C.R. Acad. Sci. U.R.S.S.*, **3**, 236.
Rice, O. K., 1940. Electronic Structure and Chemical Binding. McGraw Hill, London and New York.
Robertson, J. M., and Woodward, I., 1940. *J. Chem. Soc.*, 36.
Rosenheim, A., and Gerb, L., 1933. *Z. anorg. Chem.*, **210**, 289.
Senff, H., and Klemm, W., 1939. *J. prakt. Chem.*, **154**, 73.
Schlesinger, N., 1925. *Ber. dtsch. Gess. Chem.*, **58**, 1877.
Sugden, S., 1932. *J. Chem. Soc.*, 246.
Theilacker, W., 1937. *Z. anorg. Chem.*, **234**, 161.
Tscherniaev, I., 1926. *Ann. Inst. Platine*, **4**, 243.
Tscherniaev, I., 1928. *Ann. Inst. Platine*, **6**, 55.
Tscherniaev, I., and Gelman, A. D., 1936. *C.R. Acad. Sci. U.R.S.S.*, **18**, 181.
Tschugaeff, L., 1910. *J. Russ. Phys. Chem. Soc.*, **42**, 1472.
Tschugaeff, L., 1915. *C.R. Acad. Sc. Paris*, **161**, 563.
Tunnel, G., Posnjak, E., and Ksanda, C. J., 1935. *Z. Krist.*, **90**, 120.
Vezes, 1903. *Bl.*, **29**, 83.
Wells, A. F., 1936. *Z. Krist.*, **95**, 74.
Wells, A. F., 1938. *Z. Krist.*, **100**, 189.
Werner, A., 1893. *Z. anorg. Chem.*, **3**, 267.
Wooster, W. A., 1938. Crystal Physics, Camb. Univ. Press, Cambridge, p. 177.

METHÆMOGLOBIN FORMATION.

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INTRODUCTION.

The slow autoxidation of oxyhæmoglobin to methæmoglobin has been known since Hoppe-Seyler discovered the latter compound in 1864. Neill (1925) and Neill and Hastings (1925) drew attention to the rôle that the partial pressure of oxygen played in the reaction. They observed that the autoxidation of oxyhæmoglobin reached a maximum rate at 20 mm. oxygen pressure. At this pressure they assumed the hæmoglobin to be half saturated. The reaction was formulated as an oxidation of reduced hæmoglobin by oxygen.

Brooks (1932, 1935) examined the effect on the reaction of variables such as pH, oxygen pressure, ionic strength, specific salt effects, as well as the method of preparation of the sample of hæmoglobin used. Other variables remaining constant, he showed that the reaction was of the first order with respect to the unchanged hæmoglobin. When the partial pressure of oxygen was varied the reaction velocity reached a maximum at 19·7 mm. To explain this effect of the partial pressure of oxygen on the rate of reaction he assumed that there were two competing reactions between oxygen and reduced hæmoglobin, i.e. the addition of oxygen to form oxyhæmoglobin (oxygenation—no change of valence), and the oxidation of the ferrous iron in hæmoglobin to the ferric iron in methæmoglobin. At high oxygen pressures the reduced hæmoglobin was removed as oxyhæmoglobin, and hence the second reaction proceeded at a slower rate. On this hypothesis he derived an empirical equation which described fairly well the dependence of the rate of reaction on the oxygen pressure. He concluded that the partially oxygenated intermediates expected on Adair's hypothesis played no rôle in the reaction.

In this paper it is proposed to show that a re-examination of Brooks' experimental results, in the light of the structural interpretation of hæmoglobin proposed by Pauling (1935), can lead to a new hypothesis for the dependence of the rate of methæmoglobin formation on the partial pressure of oxygen, in which partly oxygenated intermediates play a rôle. Reasons for preferring this mechanism to that suggested by Brooks are given below.

THE STRUCTURE OF HÆMOGLOBIN.

Following on the demonstration that a molecule of hæmoglobin of molecular weight 68,000 contained four prosthetic groups, each able to combine with oxygen, Adair (1925) put forward his intermediate compound hypothesis. In this he suggested that unoxygenated hæmoglobin could combine successively with four oxygen molecules, leading to partly oxygenated intermediates Hb_4O_2, Hb_4O_4 and Hb_4O_6, as well as fully oxygenated Hb_4O_8. He found that the equilibrium between hæmoglobin and oxygen could be described by an equation

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with four equilibrium constants corresponding to the four oxygenated intermediates.

On the basis of further assumptions as to the nature of the hæmoglobin molecule, Pauling subsequently derived an equation for the equilibrium between oxygen and hæmoglobin which contained only two constants. He assumed that interaction occurred between adjacent HbO_2 groups in such a way that the free energy of addition of oxygen to hæm, $RTlnK$, is diminished by $RTln\alpha$ where such interaction occurs. If the hæms are arranged on the surface of the hæmoglobin molecule with the iron atoms at the corners of a square (square configuration) and interaction between adjacent hæm groups could occur, equation I could be derived for the equilibrium; if the hæms are arranged at the corners of a tetrahedron, each hæm equidistant from the other three, equation II holds,

$$y=\frac{Kp+(2\alpha+1)K^2p^2+3\alpha^2K^3p^3+\alpha^4K^4p^4}{1+4Kp+(4\alpha+2)K^2p^2+4\alpha^2K^3p^3+\alpha^4K^4p^4} \quad \text{I}$$

$$y=\frac{Kp+3\alpha K^2p^2+3\alpha^3K^3p^3+\alpha^6K^4p^4}{1+4Kp+6\alpha K^2p^2+4\alpha^3K^3p^3+\alpha^6K^4p^4} \quad \text{II}$$

where y equals the oxygen saturation of hæmoglobin, p the oxygen pressure in mm. mercury, K the equilibrium constant, and α the interaction constant (K and α as defined above).

Pauling (1935) and Coryell *et al.* (1939), as well as Altschul and Hogness (1940) prefer the square configuration. Optical studies by Perutz (1939), evidence from diffusion and viscometric studies (Neurath 1938), and from the asymmetry constant from sedimentation data (Svedberg 1938), all point to an ellipsoidal molecule. Pederson and Anderson (cited by Svedberg 1938) report that on dilution hæmoglobin dissociates reversibly into two equal parts, while Steinhardt (1938) has observed such a dissociation in solutions of amides. Altschul and Hogness suggest that an explanation of the salt effect on the oxygen equilibrium may be due to such dissociation. If all the hæms are assumed equivalent to one another, it is difficult to see how an ellipsoidal molecule can have the four hæms arranged tetrahedrally and yet dissociate into two parts of equal molecular size. Nor could the hæms be arranged in one plane, as demonstrated by Perutz, and still be equivalent. Hence a square configuration is more probable.

At a given oxygen pressure p, the relative concentrations of the various intermediates for the square configuration Hb_4, Hb_4O_2, Hb_4O_4, Hb_4O_6, Hb_4O_8 are as $1 : 4Kp : (4\alpha+2)K^2p^2 : 4\alpha^2K^3p^3 : \alpha^4K^4p^4$. Having solved the equation for K and α from various experimental values for y and p, it is possible to calculate the concentrations of the intermediates at various pressures. This solution is simplified by a method used by Altschul and Hogness. Since in equations I and II K and p occur to the same power while α does not, a plot of y against log Kp, where various values of α are taken, will give a family of curves, the slopes of which vary with α. A plot of y against log p for the experimental figures gives a curve which can be fitted to the nearest member of the family. This gives the nearest value for α, while the difference between log p (experimental) and log Kp (calculated) gives the value for K. Brooks' experimental results for the equilibrium are expressed in this way in Figure 1; the best agreement with equation I is found when $\alpha=3$ and $K=0\cdot0174$. Where a similar procedure is carried out with equation II (tetrahedral configuration), the experimental results can be expressed by this equation when $\alpha=2$ and $K=0\cdot0186$.

The values for α and K which fit the experimental results having been determined, it is possible to calculate the fraction of hæmoglobin which is present in each of the intermediates at a given oxygen pressure. This has been done in Table I for the square configuration at the oxygen pressures at which Brooks measured the rate of methæmoglobin formation.

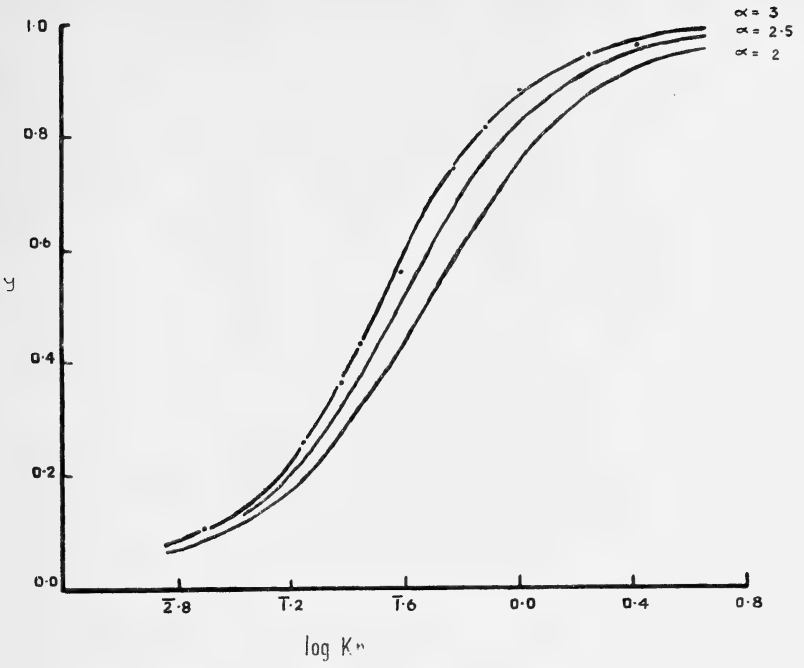

Figure 1.

Ordinate the oxygen saturation of hæmoglobin, abscissa log Kp.
Solid lines represent theoretical plots for equation I when $\alpha=2$, 2·5 and 3. Points superimposed on curve $\alpha=3$ are the results of Brooks, plotting y against log p.

Table I.

pO_2 in mm.	4·5	6·0	13·7	16·0	25·8	33·3	63·1	92·9	122	152
Hb_4 ..	0·705	0·618	0·286	0·224	0·082	0·041	0·005	0·001	0·000	0·000
Hb_4O_2 ..	0·221	0·258	0·273	0·250	0·148	0·096	0·024	0·009	0·004	0·002
Hb_4O_4 ..	0·060	0·094	0·227	0·243	0·232	0·195	0·090	0·049	0·031	0·021
Hb_4O_6 ..	0·012	0·024	0·139	0·174	0·268	0·290	0·254	0·203	0·167	0·141
Hb_4O_8 ..	0·002	0·006	0·075	0·109	0·270	0·378	0·627	0·738	0·797	0·836

It can be seen that the fraction of intermediate Hb_4O_2 increases to a maximum at about 13·7 mm. oxygen pressure, while intermediate Hb_4O_4 increases to a maximum at about 20 mm. oxygen pressure, approximately the pressure at which the rate of formation of methæmoglobin reaches its maximum. A similar calculation for the fraction of hæmoglobin present in each of the intermediates when the tetrahedral configuration is assumed leads to the same result, that Hb_4O_4 is the intermediate the concentration of which is maximal at the same pressure at which the rate of methæmoglobin formation is greatest.

The Reaction Mechanism.

Brooks had formulated the reaction as one between reduced hæmoglobin and oxygen, competing with the oxygenation of hæmoglobin to oxyhæmoglobin. It is hard to imagine how the iron atom in hæmoglobin can react in two different

ways towards oxygen, since in each case the point of attack must be on the sixth co-ordination valency of the iron. This makes it likely that the first addition compound of oxygen and hæmoglobin is the same for both reactions. Furthermore the first order rate constant does not favour the bi-molecular reaction which Brooks assumes unless the rate determining step depends on the breakdown of a particular intermediate.

Brooks had taken the intermediates into account only as reactants with oxygen. While at a constant pressure, k, the rate constant, is defined by the equation

$$\frac{dx}{dt}=k(a-x),$$

when the pressure is varied he defined the rate constant k by the equation

$$k=K_1 \text{ (intermediate) } . \ p.$$

The concentration of the intermediate (intermediate) can be written as $f(p)$, and K_1 is a constant.

From this equation follows

$$\text{(intermediate)}=\frac{k}{K_1 \, . \, p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ III}$$

As p increased k/p diminished. Hence for K_1 to remain constant the concentration of the intermediate must diminish as p increases. Calculating the concentrations of the intermediates from Adair's equation Brooks found that the only intermediate which fulfilled this condition was Hb_4. But the substitution of the values for the fraction of Hb_4, calculated in this way, did not lead to a constant value for K_1. Hence, Brooks concluded, the intermediates cannot be shown to play a rôle.

A simpler assumption for the mechanism of the methæmoglobin formation is that the rate depends on the concentration of a particular intermediate, which breaks down spontaneously into methæmoglobin. This would explain the order of the reaction without the difficulties inherent in Brooks' hypothesis, the dependence of the rate constant on the pressure being due to the variation of the concentration of the intermediate with pressure.

If this is the case

$$k=\text{(intermediate)} \, . \, K_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ IV}$$

where K_2 is a constant, and the concentration of the intermediate (intermediate) may be written as $f(p)$.

It should be noted that Brooks' formulation of the rôle of the intermediates as $k=(Hb_4) \, . \, K_1 \, . \, p$ can be written as $k=(Hb_4O_2) \, . \, K'_1$, since $(Hb_4O_2)=K(Hb_4)(p)$ where K is the equilibrium constant and $K'_1=K_1/K$. The procedure which Brooks carried out to show that Hb_4 was not a reactant according to his hypothesis also excluded the possibility that Hb_4O_2 is an intermediate on the hypothesis put forward as equation IV.

Table II shows the values of K_2 calculated from equation IV from the experimental values of k found by Brooks, and the values for the concentration of Hb_4O_4 from Table I. This is the only intermediate which gives any sort of constancy for the values of K_2, as might be expected since the other intermediates have their maximum concentrations at pressures other than the maximum pressure for the rate of methæmoglobin formation.

The above calculation has been derived from the square configuration of the hæms. If the tetrahedral configuration is used as the theoretical basis, the same intermediate, Hb_4O_4, is implicated as the one whose concentration most closely parallels the change of the rate constant with pressure. No distinction can be made between the cis and trans forms of Hb_4O_4, since their concentrations are proportional to one another at any pressure.

Table II.

pO_2 in mm.	$k \times 10^2$	a		b		k''
		(Hb_4O_4)	$K_2 \times 10^2$	(Hb_4O_4)	$K_2 \times 10^2$	
4·5	9·9	0·060	165	0·065	152	2·21
6·0	12·6	0·094	134	0·099	127	2·24
13·7	15·9	0·227	70	0·232	69	1·79
16·0	17·6	0·243	72	0·249	71	1·94
25·8	17·7	0·232	76	0·239	74	1·94
33·3	14·5	0·195	74	0·200	74	1·77
63·1	10·3	0·090	114	0·089	114	2·01

k rate constant for methæmoglobin formation (Brooks).

(Hb_4O_4) fraction of hæmoglobin as Hb_4O_4 (*a*) from Table I, (*b*) taken from Brooks' table of intermediate concentrations.

K_2 constant according to equation IV, (*a*) using (Hb_4O_4) from Table I, (*b*) using (Hb_4O_4) from Brooks' table.

k'' constant from Brooks empirical equation.

As comparison, in Table II is given the constant k'' derived from Brooks' experimental equation for the rate of methæmoglobin formation

$$\frac{dx}{dt} = k'' \cdot m \cdot (a-x) \cdot \frac{bp}{1+bp}$$

where k'' is a constant (1·95), m equals the fraction of hæmoglobin as Hb_4, $(a-x)$ per cent. hæmoglobin unoxidised at time t, and b is a constant (0·0118).

Discussion.

The conclusion that Hb_4O_4 is the intermediate which breaks down spontaneously into methæmoglobin suggests that the reaction may perhaps be formulated as follows, assuming that water is co-ordinated to a hæm group when oxygen is not.

$$[Hb_4(O_2)_2(H_2O)_2] + H^+ \rightarrow [Hb^+_4(OH)_3] + O_2 + H_2O$$
$$[Hb^+_4(OH)_3] + OH' \rightarrow [Hb_4(OH)_4]$$

The light thrown on the mechanism of the reaction by Pauling's theory is, conversely, an additional indication of the validity of the assumption of interaction between the hæms. The spontaneous formation of methæmoglobin can be added to the reactions of hæmoglobin which show hæm interaction. Coryell (1939) has shown that in the redox system hæmoglobin-methæmoglobin interaction occurs.

In the reaction between ascorbic acid and oxyhæmoglobin Lemberg *et al.* (1941) have shown that at low oxygen pressures the breakdown of oxyhæmoglobin proceeds faster than at atmospheric pressure. Here a coupled oxidation takes place where the porphyrin ring is oxidised to form choleglobin. It has not yet been possible to carry out for the latter reaction the necessary experiments which would show which intermediate, if any, is most important here.

In the latter paper it is also shown that H_2O_2 forms more choleglobin when it reacts with reduced hæmoglobin than when it reacts with oxyhæmoglobin. This result may throw light on the mechanism of the coupled oxidation. A hæmoglobin H_2O_2 compound, formed in the coupled oxidation in which H_2O_2 is attached to only two of the available hæms, may undergo oxidation of the porphyrin nucleus more readily than one in which there are also O_2 molecules attached to a molecule of hæmoglobin.

It seems likely, then, that the formation of both methæmoglobin and choleglobin can be added to the list of hæmoglobin systems (Coryell 1939) which can be best interpreted in terms of hæm-hæm interactions.

Summary.

The hypothesis put forward by Brooks to explain the dependence of the rate of methæmoglobin formation on oxygen pressure is rejected. A recalculation of his experimental results in the light of Pauling's theory of the equilibrium of oxyhæmoglobin suggests that Hb_4O_4 breaks down spontaneously to methæmoglobin. This reaction is of the first order at constant pressure. When the pressure is varied the rate depends on the concentration of Hb_4O_4.

Acknowledgments.

The author wishes to thank Dr. R. Lemberg for his help and encouragement, and Professor V. A. Bailey and Mr. Alan Maccoll, of the University of Sydney, for their help in the mathematical aspects of the problem.

References.

Adair, G. S., 1925. *Proc. Roy. Soc.* (London), A, **109**, 292.
Altschul, A. M., and Hogness, T. R., 1939. *J. biol. Chem.*, **129**, 315.
Bernal, J. D., Fankuchen, I., Perutz, M., 1938. *Nature*, **141**, 523.
Brooks, J., 1932. *Proc. Roy. Soc.* (London), B, **109**, 35.
Brooks, J., 1935. *Proc. Roy. Soc.* (London), B, **118**, 560.
Coryell, C. D., Pauling, L., and Dodson, R. W., 1939. *J. phys. Chem.*, **43**, 825.
Coryell, C. D., 1939. *J. Phys. Chem.*, **43**, 841.
Lemberg, R., Legge, J. W., and Lockwood, W. H., 1941. *Biochem. J.*, **35**, 339.
Neill, J. M., 1925. *J. Exp. Med.*, **41**, 561.
Neill, J. M., and Hastings, A. D., 1925. *J. biol. Chem.*, **63**, 479.
Neurath, H., 1938. Symposia on Quantitative Biology, 6, 196.
Pauling, L., 1935. *Proc. Nat. Acad. Sc. Washington*, **21**, 186.
Perutz, F. M., 1939. *Nature*, **143**, 731.
Steinhardt, J., 1938. *J. biol. Chem.*, **123**, 543.
Svedberg, T., 1938. *Proc. Roy. Soc.* (London), B, **127**, 1.

ERRATUM.

Page 53, in Table I, column 3, for " 24/11/27 " *read* " 24/11/37."

A NOTE ON THE ESSENTIAL OIL OF *EUCALYPTUS CONGLOBATA* VAR. *ANCEPS*.

By P. A. Berry, M.Sc.,
and T. B. Swanson, M.Sc.

Manuscript received, February 9, 1942. Read, April 1, 1942.

In connection with another investigation, a quantity of eucalyptus oil was distilled from a species of eucalypts which has now been identified as *E. conglobata* var. *anceps*.

A quantity of growing tips from this species was collected by H. J. Wiadrowski at MacGillivray, Kangaroo Island, in November, 1937, and distilled in the experimental still at American River. This species is common to the better class of soils and is associated with *E. cneorifolia*. The leaf was collected from country which had been burnt about four years earlier. A search through the literature has failed to reveal a prior publication of the constituents of this oil.

Two distillations were made, using 100 lb. leaves and growing tips for each run. Ten gallons water was used in the still for each distillation, 6 gallons of aqueous distillate collected during a 5 hours distilling period. (See Table I.)

Table I.

Distillation of Leaves.

	Distilled 23/11/37.	Distilled 24/11/27.
Yield of crude oil	0·69%	0·74%
Density 15·5/15·5°	0·908	0·907
$[\alpha]_D^{20}$	+13·37	+14·11
Ester value	4·9	2·8
Total alcohols calculated as $C_{10}H_{18}O$	6·1%	6·7%
Total aldehydes and ketones as $C_{10}H_{14}O$	1·5%	1·5%
Cineol (by ortho-cresol method)	58·0%	57·2%
Terpenes, etc., by difference (principally d-α-pinene)	34·4%	34·6%

The two distillations yielded oils of closely uniform composition. The oils were free from appreciable quantities of phellandrene (negative result with nitrosite test).

The crude oils were mixed for further work. 300 ml. of oil was shaken with resorcin solution 50% to remove cineol. In all 2,500 ml. resorcin solution was used (1,400 ml., 700 ml. and four successive portions of 100 ml.). Crude cineol recovered by steam distillation of the resorcin solution 178 ml. The oil remaining after this treatment was steam distilled, 35 ml. distillate, had the following constants. Density 15·5/15·5, 0·864, $[\alpha]_D^{20}$+42·9, contained cineol 10·2%.

Examination for Presence of Cymene.

25 ml. was oxidised at room temperature with potassium permanganate solution (20 g. in 500 ml. water) to which solid potassium permanganate was added until oxidation was complete. In all 193 g. $KMnO_4$ was used. On steam distillation only 0·2 ml. oil was obtained, indicating the absence of appreciable amounts of cymene.

Examination for Terpenes.

7·7 ml. (of 35 ml. separated above) was distilled rapidly at atmospheric pressure. Distillation commenced at 130° C. and the temperature rose quickly to 158° C. and then slowly to 163° C.

TABLE II.

Distillation of Terpene Fraction.

Fraction.	Temperature.	Time.	Yield.	$[\alpha]_D^{20}$	Density 15·5/15·5°
1	158-163° C.	3 min.	5·8 ml.	+44·3	0·864
2	163-168° C.	2 ,,	1·3 ml.	—	—

The fractions smelt strongly of pinene and the presence of d-α-pinene was suspected from the physical constants. Since the yield of nitrosochloride diminishes with increased optical rotation, the preparation of the nitrosochloride was not attempted, and oxidation with potassium permanganate at ice temperature was carried out (Gildemeister and Hoffmann, Vol. I, 2nd edition, p. 299). Three g. of fraction 1 was oxidised with 7 g. $KMnO_4$, dissolved in 90 ml. water, the mixture being kept cold in a bath of ice and water. After oxidation was complete, the mixture was filtered, washed with ether and the aqueous filtrate evaporated and acidified with sulphuric acid, the precipitated acid extracted with petroleum ether and the solvent evaporated. A thick viscous mass resulted, which did not crystallise on standing; $[\alpha]_D^{20}$ (c=5·842 in alcohol) = +13·1. This would appear to be impure pinonic acid. Semicarbazone was prepared from the crude material and recrystallised from alcohol. Melting point, 203-204° C. (melting point of semicarbazone of d-pinonic acid, 204° C.) thus confirmed the presence of d-α-pinene in the oil. The terpene fraction (see constants of steam distillation above) appears to consist principally of d-α-pinene.

SUMMARY.

The oil from the growing tips of this species consists principally of cineol (58%) and pinene, with a small proportion of alcohols, aldehydes and ketones.

We are indebted to the Commonwealth Government for a grant from the Federal Research Grant and also to Miss C. M. Eardley, M.Sc., of the Botanical Department of the Adelaide University, for the identification of the species.

Johnson Chemical Laboratories,
The University of Adelaide,
and
New England University College,
Armidale, N.S.W.

STUDIES IN METAMORPHISM AND ASSIMILATION IN THE WELLINGTON DISTRICT, N.S.W.

II. The Dynamic and Contact Metamorphism of a Group of Ultrabasic Rocks.*

By Elizabeth M. Basnett, M.Sc.†

With one map and ten text-figures.

Manuscript received, March 18, 1942. Read, April 1, 1942

I. Introduction and Previous Records.

The ultrabasic lamprophyres crop out in at least twelve sills to the east of Wellington, in the parishes of Wuuluman, Nanima and Bodangora. Although individual sills are generally narrow and of no great length (see Fig. 1), the group extends for about twelve miles in a north-south direction.

These rocks were first recorded by Matheson (1930) as lamprophyre, from the Wuuluman Road crossing on Poggy Creek. He believed that the outcrop was of limited extent and that the rock represented a " basic differentiation product of the granite magma ". Later Jones (1935) reported that the same outcrop was a small amphibolite intrusion, probably of late Silurian age.

To the south of the Wuuluman Road the lamprophyres have suffered intense dynamic metamorphism along a fault zone. This alteration is accompanied by migration of material. Although some directional structures are visible even north of the Mudgee Road, the northern part of the area suffered relatively little shearing. Furthermore the lamprophyres in part of the area were contact-altered by the Wuuluman granite (see Fig. 1). On Poggy Creek there is a small intrusion of hornblende porphyrite most likely connected with the granite, but it has not affected the surrounding lamprophyre.

II. Nature of the Intrusion and Field Occurrence.

The lamprophyres have been injected as a series of parallel sills. In the south, along Poggy Creek, they occur between the Sedimentary and Volcanic Stages of the Silurian Series, and have been folded into a northward plunging anticline, with the lavas and breccias exposed along the southern part of the crest. Along the eastern and western boundaries of the intrusion, between the edge of the granite and the Wuuluman Road, the overlying shales contain a narrow bed of banded calcareous tuff. South of the road this continues along the whole of the eastern boundary of the lamprophyre, but on the western side grades into fairly coarse non-calcareous tuff (Fig. 1). North of the Wuuluman Road, on the western edge of the granite, the sills are injected into the Sedimentary Stage above the calcareous tuff.

The sills range from a few feet to almost three-quarters of a mile in width on Poggy Creek, where folding has occurred. Occasionally, narrow veins and stringers less than an inch wide penetrate the shales. Many sills occur in the sediments west of the granite, but are visible only in creeks and gullies. Two

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† The greater part of this work was carried out at the University of Sydney during the tenure of a Commonwealth Research Scholarship.

well defined sills, approximately 18 feet wide, run parallel to the granite boundary for about one and a half miles (Locality (I) on Fig. 1). In Por. 14, Par. Bodangora there are three narrow sills and a small dyke (Locality (2) on Fig. 1), and in Por. 179, Par. Bodangora there are two sills, one about ten feet wide, the other smaller (Locality (3) on Fig. 1). In all these cases the outcrops are shown as single sills on the map.

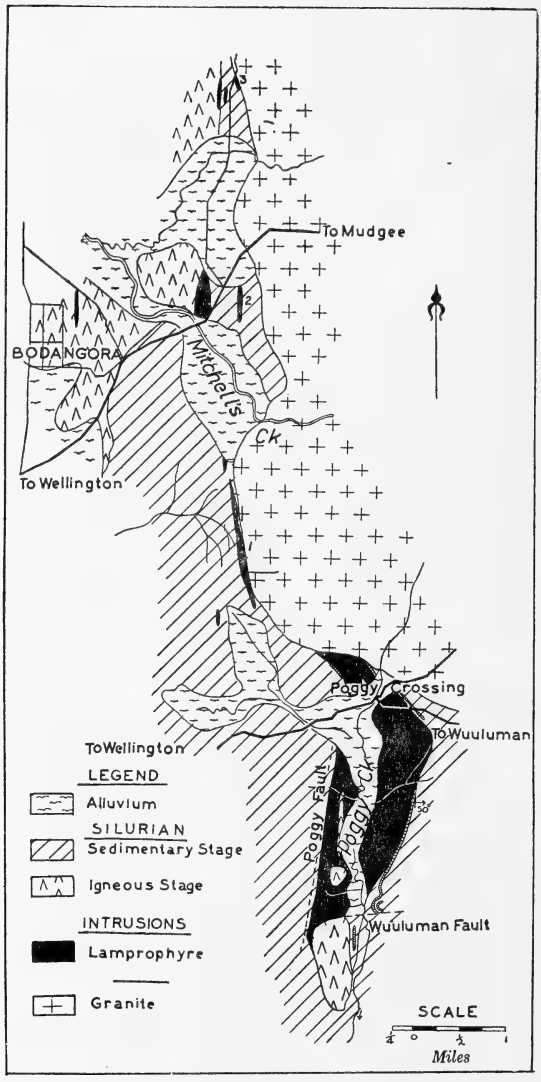

Fig. 1.

III. Petrography.

(I) The Original Lamprophyre.

Although the nature of the original rock is generally masked as a result of dynamic or contact metamorphism, some idea of the original mineralogical

constitution can be gained. There are three main types which have been classified according to their phenocrysts, namely :

(1) Augite lamprophyre (Fig. 2A).
(2) Augite-Plagioclase-Lamprophyre (Fig. 2B).
(3) Hornblende lamprophyre.

The nomenclature is discussed on page 72.

The first occurs throughout the area, the second in Por. 31, Par. Bodangora, and the hornblende lamprophyre in Mitchell's Creek a little above the Mudgee Road crossing. For the sake of brevity they will be described together.

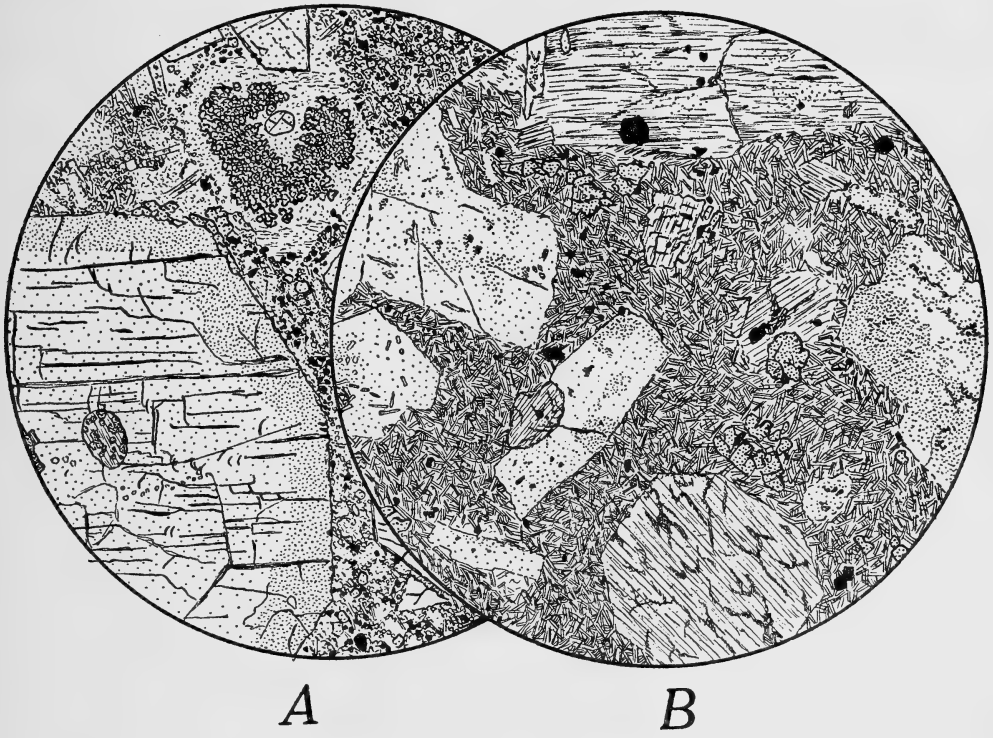

Fig. 2. The original lamprophyre.

A. *Augite lamprophyre.* The large zoned augite phenocryst shows a corroded central portion. The inclusion is a pseudomorph after olivine. Towards the top of the diagram a pyroxene phenocryst has been almost entirely replaced by chlorite and epidote. The groundmass consists of augite, fibrous hornblende, plagioclase, a little chlorite, and epidote. ×16.

B. *Augite-Plagioclase Lamprophyre.* The large plagioclase phenocrysts consist of acid plagioclase and granules of epidote. The pyroxene phenocrysts have been replaced by fibrous amphibole, with some biotite. Epidote forms fairly large crystals and grains. The groundmass consists of hornblende, biotite, some plagioclase and epidote. ×16.

The pyroxene phenocrysts vary greatly in size and abundance in the different sills, but in individual sills are fairly constant ; in some of the augite-lamprophyres they occur in two generations. The larger ones range in size from 2 mm. to 3 mm. in some sills, and up to 20 mm. in others ; those of the second generation are less than 2 mm. Glomeroporphyritic development is rare. Zoning is well shown in the larger phenocrysts (Fig. 2A), although variable even within the one rock section. The central zones are lighter in colour and only noticeable under crossed nicols, while the outer zone varies greatly in width and may have a larger extinction angle. Corrosion of the central zone is marked

(Fig. 2A), often reducing crystals to irregular grains with pseudo-inclusions of groundmass. The outer zone has generally preserved the shape of the grains, but occasionally produces crystal faces. At times this zone has been moulded on to the plagioclase of the groundmass, giving a sub-ophitic fabric, and in finer grained rocks the two may be intergrown. The colour ranges from colourless to pale greenish grey, yellow-green or light yellow-brown. The yellow-green variety is pleochroic, X=pale yellow, Y=deeper yellow, Z=pale green (X<Y=Z). Both simple and multiple twinning are common. Schiller inclusions are rare. The pyroxene is optically positive, Z $\wedge$c may be as much as 45°. In the yellow-brown varieties $\alpha=1\cdot674$, $\gamma=1\cdot703$; in the colourless and slightly green varieties $\alpha=1\cdot674$, $\gamma=1\cdot699$. The augite is therefore a diopsidic variety. The pyroxene phenocrysts of the second generation and the granules in the groundmass are generally similar in colour to the outer zone of the larger phenocrysts. These phenocrysts are not usually so well formed, but occasionally are glomeroporphyritic.

The hornblende phenocrysts of the hornblende lamprophyre are much altered by contact metamorphism. They form narrow partially corroded prisms up to 2 mm. in length, with a slight glomeroporphyritic development. They are light green and pleochroic, X=yellow green, Y=green, Z=blue-green, Z $\wedge$c 32°, optically negative, with positive elongation. Simple and multiple twinning are fairly common. In the augite lamprophyres from Poggy Creek there are small crystals (0·25 mm.) of a brownish-green amphibole (Fig. 2A). Occasionally they have a deep blue-green outer zone. Pleochroism is strong, from yellow-brown to deep blue-green, almost black. They are largely replaced by a more fibrous, pale green variety, with a strong cross parting. This alteration is probably a result of metamorphism.

In the Poggy Creek lamprophyres pseudomorphs in carbonates and chlorite, with magnetite along original cracks probably represent original olivine crystals. In other places they have been replaced by iddingsite and carbonates. (See Fig. 2A.)

Although only one sill is known with large plagioclase phenocrysts, it is probable that they were present in the lamprophyre to the east of Poggy Creek. (See p. 60.) The plagioclase phenocrysts reach 9 mm. in length and comprise about 50 per cent. of the phenocrysts in one sill (Fig. 2B). They now have a composition of $Ab_{90}An_{10}$ and contain granules of epidote, clinozoisite, and flakes of mica.

The groundmass is of rather variable texture. Generally it is fine grained and rather pilotaxitic; at times, chiefly in the augite lamprophyres, it is coarser, and the plagioclase is tabular (grainsize 0·5 mm.-1 mm.). For the most part the plagioclase shows much separation of the anorthite molecule in the form of epidote and clinozoisite. Occasionally only certain zones show alteration. Epidote is sometimes segregated into veins.

The degree of alteration due to deuteric processes is difficult to estimate because of later dynamic changes. However, in some of the least metamorphosed types, pennine may be interstitial and may replace partially or wholly some of the pyroxenes (Fig. 2A). It is associated at times with tooth-like grains of pleochroic epidote. The chlorite may be granular or platy and strongly pleochroic, $\perp$001=yellow, || 001=green. Carbonates are rarely associated with the chlorite and epidote. A local concentration of magnetite in the groundmass, giving the rock a purple colour, appears to be of deuteric origin.

(II) Types Produced by Dynamic Metamorphism.

Throughout the area the lamprophyres show more or less pronounced north-south directional structures. However, to the north of the Wuuluman Road a definite schistosity is developed only in a small creek bed in Por. 63,

Par. Bodangora. To the south marked dynamic alteration has taken place along two main faults, the Poggy and the Wuuluman (Fig. 1). The Nobby Fault, an east-west fault developed to the west, may have affected the area between the granite and the Wuuluman Road. Many minor faults also occur along Poggy Creek.

East of Poggy Creek directional structures are apparent in the field. Here the rocks resemble mineralogically the low grade green schists described by Tilley from Start Point (1923, 1938) and the retrograde types described by Wiseman (1936) from the Highlands. To the west, however, intense dynamic metamorphism has produced strongly sheared rocks. Their chemical and mineralogical composition has been modified, first by the removal of material and later by a local reintroduction of material.

(i) Schists Developed in a Sill North of the Wuuluman Road.

Plagioclase-Biotite-Hornblende-Schist. This schist, which occurs in Por. 63, Par. Bodangora, consists mainly of hornblende with some biotite, plagioclase, quartz, and occasionally sphene and calcite. It has been produced by the local crushing of a small sill.

The schistose structure is produced by the replacement of the pyroxene at first by groups of fibrous amphibole crystals obliquely arranged to the general

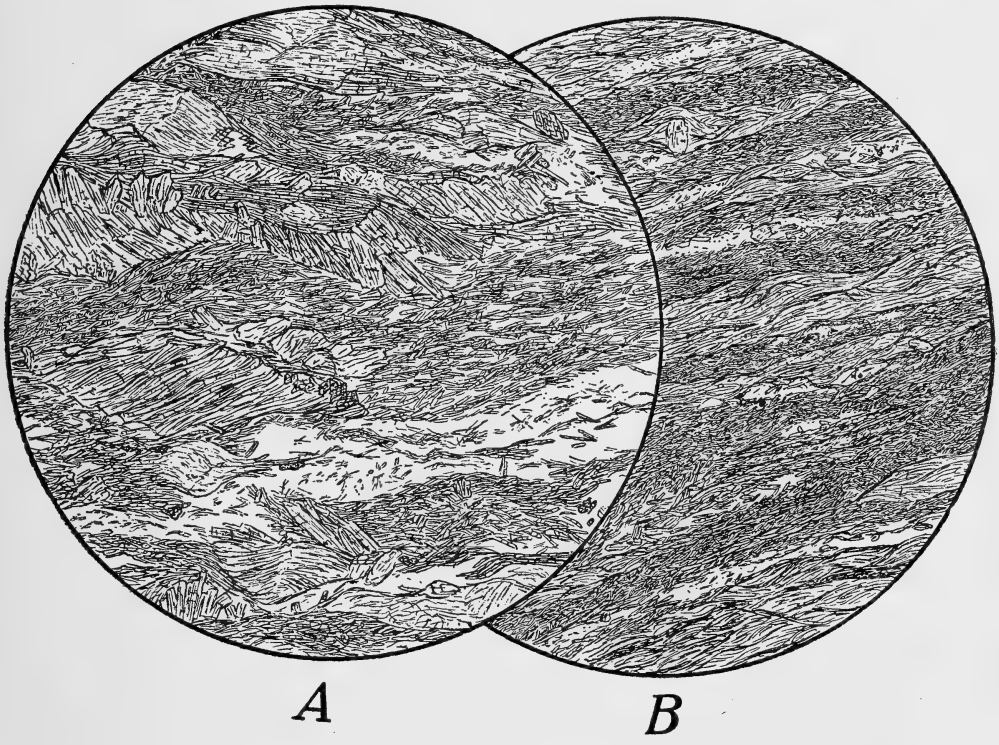

Fig. 3. Schists produced in a sill north of the Wuuluman Rd.

A. Shows to left of centre a pyroxene phenocryst replaced by amphibole fibres arranged obliquely to the schistosity. In the one above hornblende is shown developing nearly parallel to the schistosity. The groundmass consists of plagioclase, hornblende, and to the left of the figure, biotite. ×16.

B. Shows a more advanced stage. The phenocrysts have been converted into elongated, flattened lenses and continuous fracturing of the amphibole gives rise to a micro-augen structure within the lenses. Felspar forms more or less continuous narrow bands. ×16.

schistosity of the rock (Fig. 3A). At a more advanced stage, these are broken into smaller fragments and along the minute shear planes fibrous hornblende arises almost parallel to the schistosity (Fig. 3A) producing a micro-augen structure (Fig. 2B). By a continuation of this process the phenocrysts are elongated laterally, until the first-formed fibrous masses of hornblende are replaced by needle- and rod-shaped crystals, roughly parallel to the schistosity of the groundmass (Fig. 3B).

The groundmass shows progressive changes, but the adjustment is more rapid. Amphibole needles, often with flakes of biotite, are developed early and show a roughly parallel arrangement. The recrystallised plagioclase forms irregular lenses often associated with biotite and hornblende (Fig. 3A). With further crushing, the felspar, frequently accompanied by carbonates, forms narrow bands separating masses of hornblende and biotite (Fig. 3B). The two latter minerals also tend to segregate into bands.

The amphibole is very pleochroic, X=pale yellow green, Y=deeper yellow green, Z=blue green ($X<Y\leqslant Z$), optically positive, with positive elongation, $Z \wedge c = 20°$, $\alpha = 1{\cdot}640$, $\gamma = 1{\cdot}659$. Hence the composition approaches pargasite. Biotite is in places more abundant than amphibole. It is yellow and strongly pleochroic, X=pale yellow, Y=bright yellow brown, Z=dark brown ($X<Y<Z$). Granular sphene is usually present in the groundmass and may attain 1 mm. in length.

The felspar grains are clear and have irregular boundaries. Extinction on twinning $\perp 010 = 18°$, optically positive, refractive index slightly greater than that of canada balsam, composition about $Ab_{65}An_{35}$. Carbonates, where present, represent some of the released anorthite molecule.

(ii) Schists Developed in the Poggy Creek Sill.

(*a*) *Types in which there has been no Removal of Material.* To this group belong most of the altered lamprophyres cropping out to the east of Poggy Creek. Here material released during the mineralogical changes gives rise to veins and vugh-like areas, but is not removed.

In the field these rocks have slight to well developed directional structures (N. to N. 30° W.), but are not so strongly sheared as those to the west of the creek, where faults are more numerous. Occasional patches of unsheared lamprophyre indicate variations in the intensity of the directional pressure from place to place.

It is in these areas that the lowest grade dynamic types occur. The pyroxene phenocrysts are not greatly altered, but show slight fracturing and granulation, with the production of chlorite, sometimes accompanied by amphibole, along the fractures. The felspar is only slightly granulated. Finely granular epidote and clinozoisite are abundant and at times almost completely replace the felspar. Radiating and sheath-shaped aggregates of minute pale green amphibole needles occur along cleavage cracks. Larger amphibole fibres are produced as a fringe around the pyroxene phenocrysts and granules in the groundmass. Chlorite present in the groundmass is probably of deuteric origin.

In a higher grade type the phenocrysts are more granulated but only slightly altered, though the fringe of amphibole is more pronounced. However, in the groundmass the plagioclase has been entirely recrystallised. Much of the epidote is still granular but in places it has been segregated into veins. The albite forms rounded patches of clear grains or lath-shaped crystals which are sometimes twinned. The greater part of the groundmass consists of felt-like masses of tiny tremolite needles at times showing a parallel arrangement, and many granules of magnetite and sphene.

With more intense shearing a definite schistosity is developed, the chief rock types produced being :

(*a*) Hornblende-biotite-epidote-plagioclase-calcite schist.
(*b*) Hornblende-chlorite-biotite-epidote-plagioclase-calcite schist.
(*c*) Hornblende-chlorite-epidote-plagioclase-calcite schist.
(*d*) Hornblende-chlorite-epidote schist.
(*e*) Hornblende-epidote-calcite schist.

This grouping does not indicate the relative proportions of the minerals present, and considerable differences are shown within each type. The schists are not zonally arranged. Type (*b*) is the most widely developed and although mullion structure is occasionally produced in this type, types (*d*) and (*e*) are generally the most schistose. The fabric in most cases is blastoporphyritic, but rarely becomes porphyroblastic due to the development of new amphibole. To avoid repetition, these types will be described together.

The original phenocrysts have always been replaced first along cleavage cracks and shear planes, leaving patches of unaltered pyroxene (Fig. 4A). Often the pseudomorphs show lateral compression. At times crushing continued even after the early amphibolisation of the phenocrysts and along the fractures new fibrous hornblende was developed parallel to the schistosity of the groundmass. (Fig. 4D). Sometimes plications were produced (Fig. 4D). The growth of fibrous hornblende into the groundmass from the ends of the phenocrysts also increased their length parallel to the schistosity.

More often the augite was replaced by biotite and hornblende, frequently in association with epidote, clinozoisite and calcite (Fig. 4A). In these cases the amphibole shows a simple habit (110) as seen in cross section, and is strongly idioblastic against the biotite, which occurs between the elongated groups of amphibole fibres. It may be replaced by hornblende, biotite, chlorite, epidote, and calcite. Generally the chlorite and hornblende appear to arise simultaneously but sometimes the chlorite is developed later from either the biotite or hornblende. Clinozoisite may form instead of epidote. Rarely the pseudomorph consists of colourless chlorite and amphibole, with some calcite, clinozoisite, and epidote. The chlorite may be more abundant than the hornblende, but both arise simultaneously from the pyroxene. In one case the augite phenocrysts have been replaced by hornblende, quartz and calcite, with some biotite and chlorite. These pseudomorphs are practically indistinguishable from the surrounding groundmass.

In a few schists masses of magnetite associated with calcite, with or without epidote, and bounded by straight edges (Fig. 4C), may be pseudomorphs after some mineral other than augite. This may have been hornblende, for amphibole occurs in some of the least altered lamprophyres (see p. 58). The possibility that it was either olivine or hypersthene must not be overlooked, but in these cases lime would have to be introduced. Hypersthene has not been detected in the original lamprophyres.

Lime set free in the alteration of the augite may appear in epidote crystals or grains of calcite in the pseudomorphs. It may also accumulate as calcite in protected areas at the ends of the phenocrysts (Fig. 4A) or may give rise to epidote and calcite in the surrounding groundmass.

The groundmass is variable, even within the same rock type, but is usually schistose. Generally it consists of amphibole fibres, granular epidote, a little albite and occasionally quartz and calcite. At times plagioclase is abundant, while biotite and chlorite also occur in some schists. The occurrence of calcite is variable, due to its migratory character.

Some schists, particularly those to the east of Poggy Creek, contain much granular magnetite, which tends to mask the other minerals and gives the rock

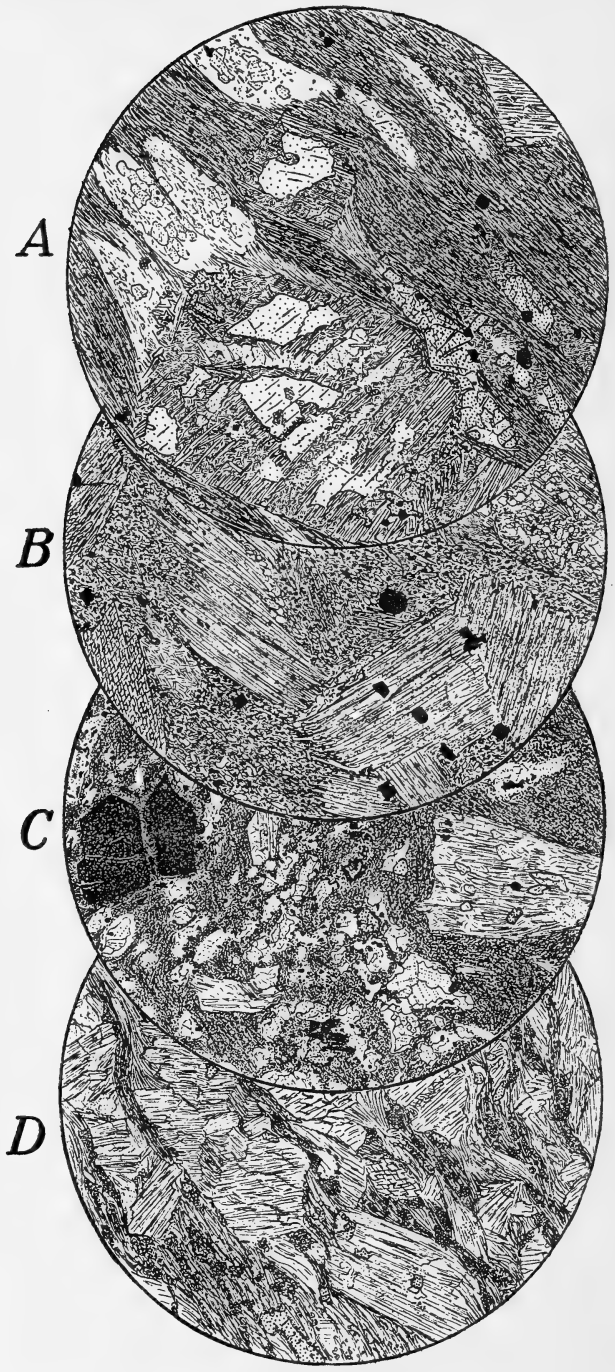

Fig. 4. Types in which there has been little or no removal of material.

A. Hornblende-Biotite-Epidote-Plagioclase-Calcite Schist. The augite phenocrysts are partially replaced by amphibole, biotite, epidote and calcite. Calcite and felspar have accumulated at the ends of the phenocrysts. The groundmass consists of fibrous hornblende, finely divided epidote, and a little magnetite. (Section cut parallel to schistosity.) ×16.

a purple colour. It is not confined to any particular type of schist, and is probably due to deuteric activity prior to metamorphism.

In many, but by no means in all of the schists, there are rounded and irregularly-shaped areas composed of plagioclase, often accompanied by calcite (Fig. 4C) or by epidote. Usually there are only a few present and these consist mainly of plagioclase. Occasionally, however, they are so numerous that the groundmass is practically obliterated. Here the calcite may form granular masses with the felspar, or may occupy the central area, while at times the mass consists of calcite with only a few rounded grains of felspar. In the latter case calcite is abundant in the groundmass, where it has often replaced the felspar. Some of these are probably pseudomorphs after plagioclase phenocrysts, others are due to segregation during metamorphism (see p. 77).

Vein- and vugh-shaped areas of calcite and large pleochroic grains of epidote are common in many schists. Some show a concentration of magnetite towards the edges and these may be of deuteric origin. Generally the epidote veins are roughly parallel to the schistosity.

The pyroxene is that of the original lamprophyre which has already been described (see p. 57).

The amphibole occurs as pseudomorphs after augite, as fine needle-shaped crystals in the groundmass, and occasionally as porphyroblasts (Fig. 4B). It often forms fine needles when associated with calcite (Fig. 4B), and fibres commonly grow into the calcite from the replaced pyroxene crystals. It ranges from colourless to green and varies slightly even within the one slide. In schists with an abundance of magnetite, the amphibole is pale green to colourless, and crowded with small inclusions of iron ore. The green variety is strongly pleochroic, X = pale yellow, Y = green, Z = blue green. It is always optically negative, with positive elongation, but $Z \wedge c$ ranges from 19° in the colourless types to 23° in the green varieties. $\alpha = 1 \cdot 603$ to $1 \cdot 643$, $\gamma = 1 \cdot 634$ to $1 \cdot 663$. This indicates a composition range from tremolite to pargasite.

Biotite is present in the pseudomorphs after pyroxene, also in the groundmass, and occasionally extends into the latter as thin parallel plates from the extremities of the phenocrysts. It is brownish green in colour and strongly pleochroic, X = pale yellow, Y = yellow green, Z = grey green ($X < Y \leqslant Z$).

Chlorite occurs in association with amphibole and biotite in the replaced phenocrysts and groundmass. Mostly it is pale green and pleochroic, with leather brown interference colours. Rarely it is colourless, shows low first order interference colours and is optically positive, with $\beta = 1 \cdot 582$. This variety is associated with the colourless amphibole. Both belong to the pennine group.

Plagioclase is abundant in the groundmass of some schists, but in others it is partially or completely replaced by amphibole. It may be slightly clouded (composition $Ab_{88}An_{12}$), or may be recrystallised as clear grains and lath-shaped crystals (composition $Ab_{95}An_5$). Twinning is not uncommon.

B. Hornblende-Chlorite-Biotite-Epidote-Plagioclase-Calcite Schist. Hornblende occurs as needles and fibrous masses in areas rich in calcite (top right of diagram) and towards the left is one of the larger porphyroblasts. Calcite, plagioclase and some quartz are irregularly distributed. (Section cut across schistosity.) ×16.

C. Hornblende-Chlorite-Epidote-Plagioclase-Calcite Schist. The augite phenocrysts have been replaced by chlorite and amphibole, with some calcite and epidote. Other phenocrysts are replaced by magnetite and calcite. There are irregularly-shaped patches of calcite and plagioclase in the groundmass. The groundmass consists of amphibole and much finely divided magnetite. (Section cut across the schistosity.) ×16.

D. Hornblende-Epidote-Calcite Schist. This diagram shows fracturing of the amphibolised phenocrysts and a further development of amphibole more nearly parallel to the schistosity. Calcite collects in areas of least stress. The groundmass is composed of amphibole and granular epidote. (Section cut across the schistosity.) ×16.

The epidote is generally strongly coloured, sometimes with a more ferriferous core. It shows well developed twinning, and generally negative elongation.

Calcite is variable in amount and tends to accumulate in areas of least pressure. Staining tests indicate that neither dolomite nor siderite is present, but some of the calcite has been iron-stained. It often contains minute needles of amphibole or flakes of chlorite which have developed *in situ*. Grains of quartz are present in the groundmass of a few schists and along the edge of the replaced pyroxenes.

(*b*) *Types in which there has been Transfer of Material.* To the west of Poggy Creek, in the zone of faulting and shearing, dynamic changes have been accompanied by the removal, in solution, of material released during the resultant mineralogical reactions. At a late stage these solutions were reintroduced in certain areas to give rise to further mineralogical changes with the production of new structures.

The rocks may be divided into two groups : (i) those with no later addition of material, (ii) those with a reintroduction of material.

(i) *Those with no Later Addition of Material.* The rocks which have suffered least removal of material are the widely distributed *tremolite-pennine-schists.* In all cases the ferro-magnesian phenocrysts have been laterally compressed and completely replaced by amphibole and chlorite (Fig. 5A). The amphibole is colourless to slightly bluish green, faintly pleochroic, optically negative with positive elongation, $Z \wedge c = 19°$, $\alpha = 1 \cdot 621$, $\gamma = 1 \cdot 644$. Thus it is a member of the tremolite-actinolite series. The chlorite forms groups of interlocking green flakes and is a pennine variety which is strongly pleochroic, $\perp 001$ = yellow green, $\| 001$ = blue green, $\beta = 1 \cdot 591$.

Lime released in the replacement of the pyroxene may be removed or may give rise to highly pleochroic grains of epidote. The groundmass is almost entirely composed of minute rod- and needle-shaped crystals of tremolite with a few flakes of chlorite, small crystals of magnetite and many minute grains of sphene.

In a more altered type with stronger schistosity there has been a greater removal of material, principally of lime, and the phenocrysts are replaced by interlocking fibres of pennine. The length of these pseudomorphs may be up to six times the breadth. The groundmass consists of tremolite and chlorite, with tiny granules of epidote.

Another type shows a greater development of pennine but less tremolite, while a member of the serpentine group becomes important ; thus *pennine ferroantigorite-tremolite schists* are developed (see Analysis II, Table II). These crop out along Poggy Creek. The large phenocrysts have been completely altered, but there are still remnants of the smaller ones, which were probably protected from shearing (Fig. 5B). The latter have a light coloured outer zone and show sporadic alteration to chlorite. The large pseudomorphs have been flattened and elongated parallel to the schistosity, but only rarely do the crystals appear to have been shattered in the process. The pseudomorphs have green chlorite in the central areas, surrounded by colourless chlorite. This is due to zoning in the original augite. The groundmass now consists of colourless chlorite, with a small amount of amphibole, tiny crystals of magnetite, and much finely divided epidote. It is traversed by wide, irregular areas of colourless chlorite, sometimes associated with a green variety (Fig. 5B). These two chlorites form 80 to 90 per cent. of the rock. The green variety, present chiefly in the phenocrysts, is markedly pleochroic, X and Y = blue green, Z = yellow green ($X = Y < Z$). It shows abnormal interference colours and $\beta = 1 \cdot 595$. This indicates an aluminous variety belonging to the pennine group. The colourless type is optically negative and has positive elongation, $\alpha = 1 \cdot 610$, $\gamma = 1 \cdot 619$. Hence it is

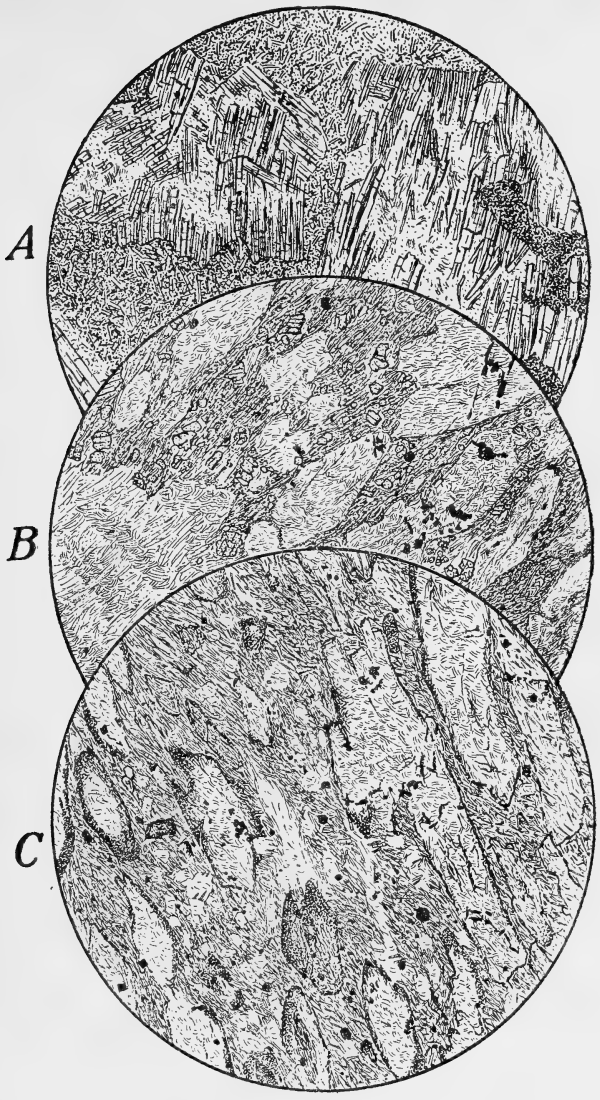

Fig. 5. Types which show a removal of material.

A. *Tremolite-Pennine Schist.* The original phenocrysts have been replaced by tremolite and pennine. To the left of the diagram, interpenetration twinning of the original crystal is preserved. Corrosion is shown to the right. The groundmass consists of rod-shaped crystals of tremolite, flakes of chlorite and much granular epidote. (Section parallel to schistosity.) ×16.

B. *Pennine-Ferroantigorite-Tremolite Schist.* Small augite phenocrysts are only partially altered to chlorite. The larger ones have been completely replaced. The groundmass consists of ferro-antigorite, much finely divided epidote, magnetite and tremolite. In the lower left-hand corner is an area consisting of fibrous ferroantigorite and flakes of pennine. (Section across schistosity.) ×16.

C. *Tremolite-Antigorite-Talc Schist.* The small phenocrysts are replaced by antigorite. The larger ones now consist of antigorite with talc, tremolite and magnetite in an irregular outer zone. The groundmass is composed of tremolite and antigorite, with crystals of magnetite. (Section across schistosity.) ×16.

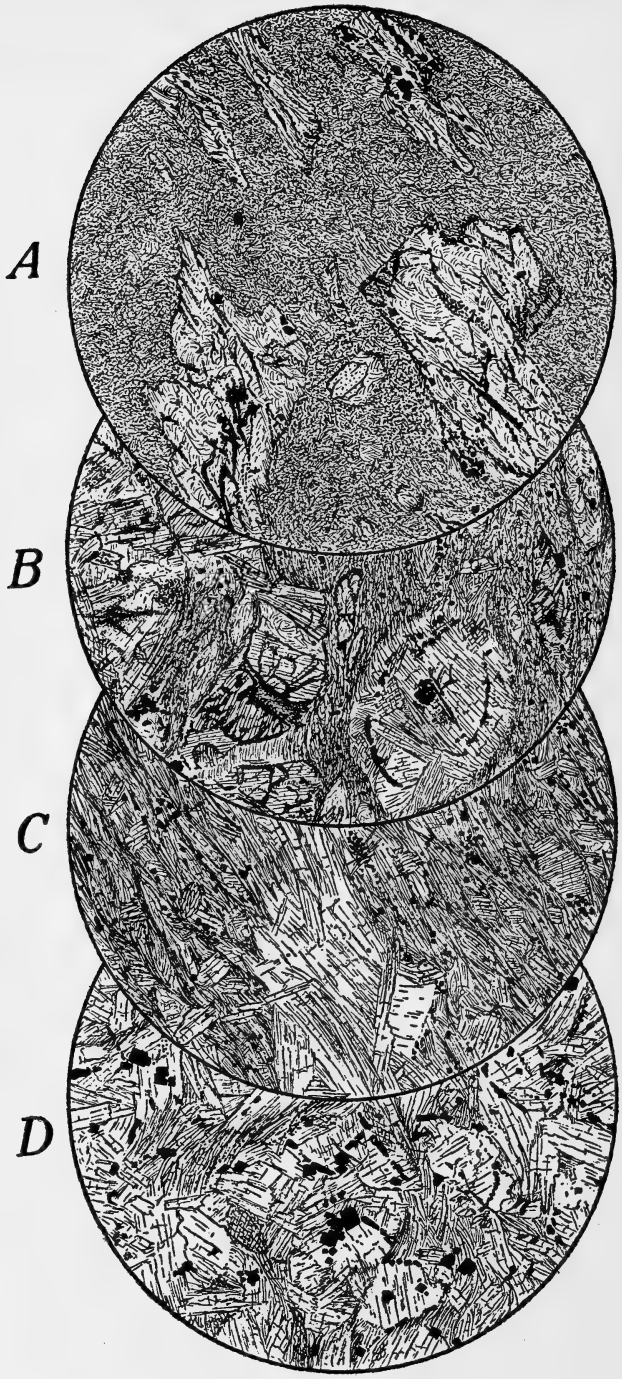

Fig. 6. Changes brought about by the reintroduction of material.

A. *Antigorite-Pennine Schist.* The phenocrysts are replaced by pennine with antigorite in the outer zone. Iron ore is abundant. Remnants of the smaller phenocrysts still persist. The groundmass consists of antigorite, finely divided iron ore, a little tremolite, and epidote. ×16.

a ferroantigorite member according to Winchell (1927). The amphibole is developed as fine, needle-shaped crystals arranged in sheath-like groups in the groundmass. It is almost colourless and is optically negative, with positive elongation; $Z \wedge c = 17°$. It appears to belong to the tremolite-actinolite series.

The *tremolite-antigorite-talc schists* (Fig. 5C) crop out along the fault zone and have been much sheared. Here pennine is absent, tremolite and antigorite are very variable and talc has been extensively developed. The large replaced phenocrysts usually have an outer zone of irregular width consisting of abundant granular magnetite and fine fibrous actinolite, often with talc (Fig. 5C). Antigorite accompanies the actinolite and talc in the central zone, and sometimes there are fine dust-like inclusions of magnetite. The smaller phenocrysts are replaced by flakes of colourless to pale green antigorite which is optically negative, with positive elongation, $\beta = 1 \cdot 575$. The groundmass is now composed of small rod- and needle-shaped crystals of tremolite, often with frayed terminations, $Z \wedge c = 22°$, $\alpha = 1 \cdot 604$, $\gamma = 1 \cdot 636$. Irregular patches of antigorite ($\beta = 1 \cdot 567$) and magnetite also occur.

On the banks of a small eastern tributary of Poggy Creek, in Por. 48, Par. Nanima, this rock type forms nodules (1 mm. to 150 mm.) surrounded by sheared and plicated masses of chlorite. The chlorite is veined by coarse, granular calcite, sometimes accompanied by a little chlorite and tremolite.

In the southern part of Por. 48, Par. Nanima, on Poggy Creek, the rock has practically no tremolite, very little epidote and is essentially an *antigorite-pennine schist* (Fig. 6A). Pennine is only present in the central portion of the phenocrysts. The groundmass consists of fibrous masses of antigorite, abundant finely divided iron ore, very small amounts of fibrous amphibole and minute grains of epidote.

(ii) *Those with a Reintroduction of Material.* The types produced as a result of a later reintroduction of material are restricted to a small area on Poggy Creek in the south of Por. 48, Par. Nanima, where they form elongated lenses (over 20 feet long by up to 6 feet wide) and nodules, associated with antigorite-pennine schists (see above and Fig. 6A). The latter rocks have suffered much lateral compression and tend to cleave readily. Where there has been an addition of material from solutions, tremolite has developed and the rocks have gradually lost their schistosity and become converted into medium-grained, compact, tremolite rocks. In this way lenses of the compact rocks have been produced in the midst of extremely schistose chloritic ones.

Tremolite is produced first in the chloritic pseudomorphs of the original phenocrysts as short stout prisms and fibrous aggregates up to 2 mm. in length. It also extends into the surrounding groundmass as large rounded xenoblastic porphyroblasts which cut across the schistosity. The original outline of the phenocryst is indicated by aggregates of small magnetite crystals (see Fig. 6B). Cracks along which alteration to chlorite took place are also preserved by parallel bands of magnetite grains. These have not been obliterated by the later development of tremolite (Fig. 6B). Masses of talc occur between the groups of tremolite crystals. Remnants of pennine and less frequently of antigorite, still persist. The chlorite pseudomorphs have not all been affected at the same time; some have been completely replaced, while in others tremolite may be

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B. Large rounded porphyroblasts of tremolite are replacing earlier formed chloritic pseudomorphs. The outline and cracks along which the earlier alteration to chlorite took place are still preserved by lines of magnetite crystals. The groundmass consists of antigorite and a little tremolite. ×16.

C. Masses of tremolite are developing across the schistosity of the groundmass. The chloritic pseudomorphs have been entirely replaced. Crystals of magnetite are abundant. ×16.

D. Replacement is practically complete; the rock now consists of compact masses of tremolite. Magnetite forms large crystals. A little pennine still remains. ×16.

absent or represented only by an occasional crystal (Fig. 6B). The developing tremolite tended to replace rather than to displace the groundmass. In the early stages the groundmass was unaffected except for the development of a little tremolite and the recrystallisation of iron ore.

With further addition the replacement of the first-formed pseudomorphs was carried almost to completion. At this stage masses of tremolite developed across the schistosity in the groundmass (Fig. 6C) and larger magnetite crystals formed. Talc still occurred in the groundmass while some antigorite and pennine still persisted.

As this process continued the rocks lost their schistose structure and became converted into compact masses of tremolite with large crystals of magnetite and only small quantities of pennine (Fig. 6D). Talc disappears.

In the earlier stages veins of tremolite pass out as long root-like masses into the groundmass, replacing it, and surrounding small rounded aggregates of pennine.

(iii) Types Produced by Contact Metamorphism.

Some time after or towards the close of the period of dynamic metamorphism, the lamprophyres were intruded and metamorphosed by the Wuuluman granite. These contact-altered types may be divided into a felspathic and a non-felspathic group. Directional structures are still visible but in most cases a superimposed granoblastic fabric is partially developed. Occasionally all schistosity is obliterated.

(*a*) *Non-felspathic Types.* These rocks are largely composed of hornblende and may be called amphibolites. There are several distinct types:

(i) Amphibolite (Fig. 7A).
(ii) Pleonaste Amphibolite (Fig. 7B).
(iii) Epidote Amphibolite.
(iv) Epidote-Biotite Amphibolite.
(v) Diopside Amphibolite (Fig. 7C).

The amphibolite crops out in the east of Por. 63 and the north of Por. 69, Par. Nanima. The pleonaste amphibolite is developed in three sills in Por. 14 Par. Bodangora, and a narrow vein about one foot wide in Por. 69, Par. Bodangora. The epidote amphibolite occurs in Pors. 3 and 83, Par. Bodangora, both outcrops belonging to the same sill, although the intervening area is covered by alluvium. The epidote-biotite amphibolite comes from Pors. 110, 111, Par. Nanima, and the diopside amphibolite from a sill actually on the granite contact in the south-western corner of Por. 179, Par. Bodangora.

The porphyritic fabric is usually preserved. The original pyroxene phenocrysts are replaced to varying degrees by amphibole, as in the dynamically metamorphosed types. Where amphibolisation is complete the outline, twinning and zoning of the replaced mineral are sometimes preserved. Iron ore set free during this process may accumulate around remnants of pyroxene, or form granules of magnetite in the hornblende (Fig. 7A). There is often a fringe-like growth of amphibole around the pyroxene phenocrysts, which may be paler than the amphibole replacing the pyroxene (Fig. 7A).

In the epidote amphibolite clinozoisite is in places more abundant than epidote. These minerals form rounded and elongated granular masses (3 mm. $\times$ 5 mm. max.) associated with a colourless mica, some colourless chlorite and a little felspar. They probably represent replaced plagioclase phenocrysts. In the epidote-biotite amphibolite from Pors. 110 and 111, Par. Bodangora, the biotite is green and epidote forms crystals up to 1 mm. long. Dark green pleonaste is produced in the groundmass of the pleonaste amphibolite either as xenoblastic grains against the actinolite, or as groups of grains in patches of chlorite (see Fig. 7B). Generally magnetite is abundant.

The amphibole replacing the pyroxene forms long thin fibres. In the groundmass it varies from felt-like masses of minute fibres, often with frayed terminations, to interlocking crystals 1 mm. in length. It ranges from colourless to pale blue green, but in the epidote amphibolites it is more yellow. Changes

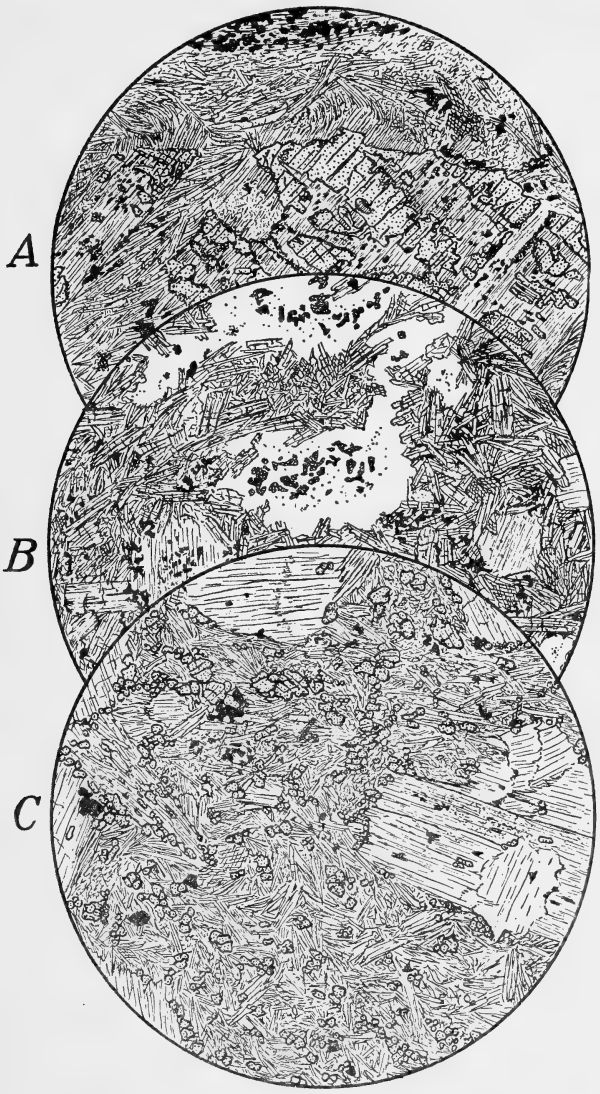

Fig. 7. Non-Felspathic amphibolites produced by contact metamorphism.

A. Amphibolite. Note the development of amphibole along cracks and cleavages in the pyroxene, and the growth of fibrous masses from the ends of the crystals. The groundmass consists of fibrous amphibole and chlorite. ×16.

B. Pleonaste-Amphibolite. The pyroxene phenocrysts are entirely replaced by tremolite and partially obliterated. Pleonaste granules occur in the irregularly shaped masses of chlorite. ×16.

C. Diopside-Amphibolite. The phenocrysts have been entirely replaced by amphibole. The groundmass consists of fibrous amphibole, grains of diopside, and a little chlorite. ×16.

in colour are seen even in one rock section. Outgrowths of hornblende from the pseudomorphs may be green at the ends, but practically colourless adjacent to the pyroxene. Pleochroism is often marked, X=colourless to pale yellow, Y=deeper yellow green, Z=blue green ($Z \geqslant Y > X$). The colourless and blue-green varieties are optically negative, with positive elongation, $Z \wedge c = 14°$ to 24°, $\alpha = 1 \cdot 622$, $\gamma = 1 \cdot 648$. They therefore belong to the tremolite-actinolite series, the larger extinction angle being indicative of high magnesia (Larsen and Berman, 1934). In the yellow green variety present in the epidote amphibolite $Z \wedge c$ may be as large as 30°, and $\alpha = 1 \cdot 628$, $\gamma = 1 \cdot 656$. The negative sign and large extinction angle suggest that it is probably closer to pargasite. Occasionally crystals up to 2 mm. long have a brown pleochroic core in which there is much magnetite. This possibly indicates an original hornblende.

Chlorite is often developed. In the pleonaste amphibolite it may form large round patches (0·5 mm. to 2 mm. in diameter) (Fig. 7B). It is colourless to faintly green, is optically positive and $\beta = 1 \cdot 585$. In other cases it is green and shows ultra blue and leather brown interference colours. Both belong to the pennine group.

Grains of diopside up to 0·25 mm. in diameter are developed as a result of contact metamorphism (see Fig. 7C). They are colourless, optically positive, $Z \wedge c = 39°$ and 2V is large. It comprises as much as 50 per cent. of the groundmass but is rare in the replaced phenocrysts except along fractures.

Magnetite is fairly abundant, especially in the spinel amphibolite. Sphene may be present, also fractured crystals of apatite showing a purplish-grey central zone.

(*b*) *Felspathic Types.* These are much less common in the contact zone than are the non-felspathic amphibolites. They crop out chiefly along the southern boundary of the granite, but in Por. 14, Par. Bodangora almost on the contact, there is a narrow sill about one foot wide.

As in the previous types blastoporphyritic fabric and relict structures are common (Fig. 8B), while the Bodangora specimen is blastophitic (see Fig. 8A). There is only a local development of a true granoblastic fabric.

Amphibolisation of the phenocrysts is similar to that already described for the non-felspathic varieties. Hornblende may also develop as grains and stout crystals up to 0·25 mm. in length round the edge of the phenocrysts (Fig. 8A), while some are completely replaced in this way.

The type from Bodangora originally had a fairly coarse-grained groundmass with plagioclase crystals up to 2 mm. long. The felspar is often clouded, or contains minute needles of hornblende (see Fig. 8A). Occasionally a granoblastic fabric has been produced. In the southern area the groundmass is entirely recrystallised, but still shows directional structures (Fig. 8B).

Along the southern boundary of the granite there are a few vugh-like areas produced either by deuteric alteration or by dynamic metamorphism. These now consist of an outer ring of magnetite grains or blue green hornblende followed by plagioclase and quartz with pleochroic epidote in the centre (Fig. 8B). Biotite may also be developed.

The amphibole is yellow green, strongly pleochroic, X=yellow green, Y=dark yellow green, Z=dark bluish green ($Z \geqslant Y > X$), $Z \wedge c = 27°$, optically positive with positive elongation, $\alpha = 1 \cdot 641$, $\gamma = 1 \cdot 662$. It therefore has a composition near pargasite and is a more aluminous variety than that found in the majority of the non-felspathic amphibolites.

The recrystallised plagioclase is only occasionally twinned, is optically negative, with extinction $\perp 010 = 21°$; hence it is andesine ($Ab_{61}An_{39}$). Plagioclase which has not been recrystallised is slightly more basic and generally shows undulose extinction.

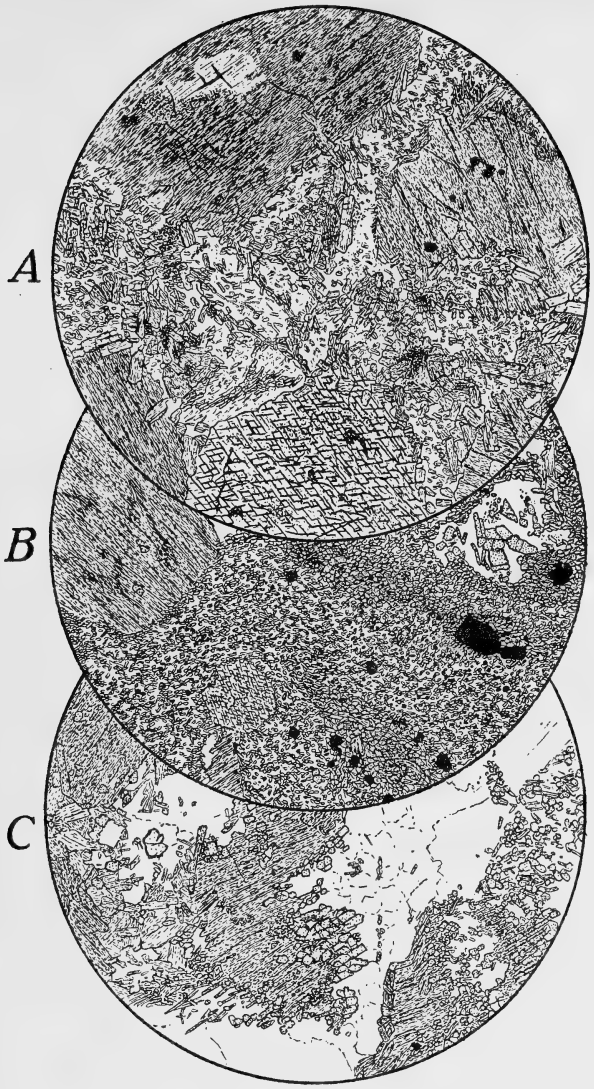

Fig. 8. Felspathic amphibolites produced by contact metamorphism.

A. Augite phenocrysts have been almost entirely replaced by amphibole. Small crystals of hornblende are developing around and through the replaced phenocrysts. In the top right quadrant the phenocryst shows blastophytic relations to the surrounding felspar. Original felspar laths are still visible, but contain many small rods and needles of hornblende. To the left of the figure a granoblastic fabric is locally developed. ×16.

B. This rock shows remnants of a schistose structure produced during dynamic metamorphism, but a granoblastic fabric is beginning to develop. The phenocrysts are replaced by amphibole. In the top right-hand corner is a vugh which is now replaced by plagioclase and epidote with an outer zone of amphibole. ×16.

C. Hybridised aplite vein. Note irregular and indefinite boundaries to the vein. Diopside is developing around the edges and through a mass of hornblende which has been practically surrounded by aplite. ×16.

Magnetite occurs as small crystals, which may reach 1 mm. in length. Granular sphene is sometimes developed. Epidote and clinozoisite granules are formed in the groundmass.

At Poggy Crossing the felspathic type is banded with a rock containing very little felspar. It has been strongly sheared and consists chiefly of a more blue green amphibole associated with brown biotite. Epidote and some biotite occur in patches throughout the rock and also in the replaced phenocrysts. It seems that these bands have suffered considerably from the earlier dynamic metamorphism but were not greatly altered by the later contact metamorphism.

In the contact altered hornblende lamprophyre the amphibole has been partially replaced by brown pleochroic biotite, epidote, and carbonates. Where a blue green amphibole is produced in association with the biotite the replaced phenocrysts were probably augite. Small felspar phenocrysts are still visible, but show undulose extinction, clouding or contain needles of amphibole, flakes of biotite and grains of epidote. The groundmass consists of plagioclase, needles and rod-shaped crystals of amphibole, flakes of biotite, and granular epidote. Veins of epidote and carbonates are common.

(iv) Hybridised Aplite Veins.

In the region between the Wuuluman Road and the southern boundary of the granite, the contact-altered lamprophyres have been intruded by large numbers of aplite dykes which do not appear to have been hybridised. However, these have given rise to small veins, often less than 2 mm. across, which penetrate the lamprophyre and show marked signs of hybridisation.

The constituent minerals of the aplite are quartz, microcline, plagioclase ($Ab_{85}An_{15}$), and small quantities of biotite and magnetite; sphene and apatite are rare. Quartz and microcline are extremely abundant. At times they are intergrown, the latter forming plates up to 4 mm. across.

The constituent minerals of the veins are microcline, plagioclase, diopside, hornblende, and small quantities of quartz; apatite and sphene are fairly abundant; biotite is not developed. The fabric is allotriomorphic granular to slightly monzonitic. Solid material, chiefly hornblende with some felspar, is incorporated in the veins and together with diopside, produced *in situ*, may occur between lath-shaped crystals of felspar developed from the hybrid magma (Fig. 8c). In other veins the felspar, diopside, and hornblende form granular masses. Where potash felspar is more abundant than plagioclase, the veins are narrow and ferromagnesian minerals are rare. In some parts of the veins sericite is developed in great quantities, often entirely replacing the felspar.

Diopside forms allotriomorphic to subidiomorphic grains, and tends to be more abundant towards the edges of the veins (Fig. 8c). It also develops in the hornblende of the surrounding lamprophyre. In these cases the boundaries of the veins are very indefinite (Fig. 8c). Where they traverse amphibolised phenocrysts, diopside is formed along the broken edges, and may extend right across the fracture. Occasionally the phenocrysts are almost entirely replaced. The diopside is pale green with a slight bluish tinge, non-pleochroic, optically positive, and $Z \wedge c = 43°$.

These veins occur in an area which has been impregnated by copper-bearing solutions. Some of the ferromagnesian minerals both of the lamprophyres and the veins have been attacked and partially replaced by copper carbonates.

IV. Nomenclature.

As all these rocks have been metamorphosed to some extent, the naming of the original rocks is difficult. They were first called lamprophyres by Matheson (1930), and in hand specimen this name is very suitable. In this paper the name

is still used, but it is prefixed by the names of the dominant phenocrysts (see p. 57). The augite-plagioclase lamprophyres could possibly be called porphyrites, and in one locality an augite lamprophyre which has an ophitic fabric might be termed a porphyritic dolerite, except that the felspar is rather tabular.

Chemical analyses have been made of three contact altered augite lamprophyres (Table I, columns I, II, III). They all contain high lime and magnesia, with low alumina and alkalies, indicating an ultrabasic composition. The norm shows a considerable percentage of olivine, and pseudomorphs after olivine are present in some rocks. These analyses do not compare closely with those of any lamprophyres, most of which have higher alkalies and lower magnesia and lime. They agree best with an olivine gabbro from the Ural Mts. (Table I, column IV), and a dolerite from Rhonegebirge (Table I, column V). They compare mineralogically with the original descriptions of augitites as defined by Doelter, but these are volcanic types with a glassy groundmass. No augitite listed by Iddings agrees closely with those of the Wellington rocks. So the most suitable name for these rocks still seems to be lamprophyre.

Table I.

	I.	II.	III.	IV.	V.
SiO_2	45·49	47·52	49·24	47·68	49·92
Al_2O_3	10·49	12·50	13·85	11·43	13·39
Fe_2O_3	6·44	1·08	4·88	0·16	8·07
FeO	4·36	6·26	6·55	8·90	4·82
MgO	18·48	16·50	8·34	14·81	6·13
CaO	10·72	13·07	10·94	12·48	10·68
Na_2O	0·89	0·46	2·55	1·01	2·83
K_2O	1·25	0·92	1·32	0·52	1·11
H_2O+	1·55	0·85	0·72	2·22	0·94
H_2O-	0·11	—	0·16	—	—
TiO_2	0·36	0·67	0·62	0·59	1·80
P_2O_5	0·24	tr.	0·31	0·00	1·06
MnO	0·15	0·14	0·17	0·07	—
Total	100·53	99·97	99·65	99·87	100·75
Sp. Gr.	3·10	3·13	3·09		

I. Spinel Amphibolite. Por. 14, Par. Bodangora. Anal. E. M. Basnett.

II. Epidote Amphibolite. Por. 83, Par. Bodangora. Anal. M. J. Colditz.

III. Felspar-bearing Amphibolite. Wuuluman Road Crossing on Poggy Creek. Anal. E. M. Basnett.

IV. Olivine Gabbro. Ural Mts. Anal. Pisani. A Lacroix. *N. Arch. Mus.*, 1911, **3**, p. 114.

V. Dolerite, Rhonegebirge. Anal. P. Schmidt, *Neues Jahr.*, 1905, II, p. 213.

V. Petrogenesis.

(i) Physical Conditions of the Invading Magma.

The lamprophyres contain large numbers of pyroxene phenocrysts which in some sills form more than fifty per cent. of the rock. The nature of these phenocrysts (see p. 57) suggests that during the early stage of their formation the crystals grew slowly in a constantly changing environment, and towards the

end of crystallisation they became unstable and hence were strongly resorbed. The deposition of the outer zone without later resorption indicates fairly stable conditions in the final stage of their formation. This may be explained if the phenocrysts of the first generation were well crystallised before the injection of the magma. The change in physical and chemical conditions caused by injection into the upper crust must have resulted in strong resorption. After emplacement the establishment of stable conditions once more would enable further deposition to take place around the corroded phenocrysts.

A large proportion of the sills have a fine grained groundmass, suggesting rather rapid cooling. This would not allow large zoned augite phenocrysts to develop *in situ*. Also, there are no signs of chilled margins, and phenocrysts at the edges are as large as those throughout the mass, while tiny veins $\frac{1}{2}$ inch wide contain phenocrysts up to $\frac{1}{4}$ inch across (Fig. 9). Hence it is concluded that, at the time of injection, the magma was crowded with phenocrysts formed in the intratelluric reservoir.

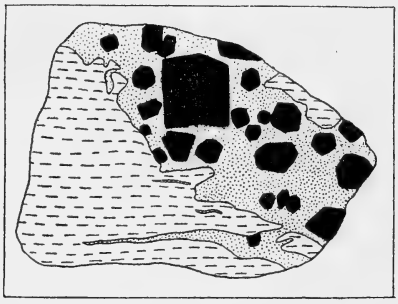

Fig. 9.

A diagram of a small vein intruding sandy shales. Note size and abundance of phenocrysts, and their presence at the edge of the vein, the lack of chilled margins, and the presence of narrow stringers through the intruded shale. N.S.

That such a magma could be injected over so wide an area and even in veins only half an inch in width must mean, either that it was extremely fluid and cooled rapidly after injection, or that it was injected into very soft sediments. The lamprophyres intrude sediments overlying the Silurian andesites, and are believed to be consanguineous with the lavas. This suggests that when injection occurred the sediments were soft or only partially consolidated, and that the weight of overlying strata could not have been great. The presence of water in the sediments may also have helped to keep the magma fluid during its injection.

(ii) Dynamic Metamorphism.

(a) Structural Changes.

The dynamic alteration of the lamprophyres resulted from local faulting, probably at no great depth in the earth's crust. The introduction of solutions along the fractures made possible the mineralogical changes already described. These two factors are together responsible for the structural changes.

In the rare cases where the original phenocrysts show shattering there has been little mineralogical adjustment. Generally, however, they have yielded by the development of new minerals, with the result that a blastoporphyritic fabric exists in rocks now entirely reconstituted mineralogically. As a result of the replacement of the phenocrysts (see petrography) under pressure they

DIAGRAM SHOWING THE EFFECT OF DYNAMIC METAMORPHISM ON THE LAMPROPHYRE FROM THE POGGY CREEK SILL.

Increasing Stress ——————→ Diminished Stress

	The Original Rock.	Types in which there is No Removal of Material.	Types in which there is removal of material. (a) With no Later Addition of Material.	Types in which there is removal of material. (b) With a Reintroduction of Material.
Physical Characteristics.	Massive and Porphyritic.	Slight to strong schistosity. Phenocrysts laterally compressed.	Highly schistose and easily cleaved. Phenocrysts more flattened.	Gradual loss of schistosity and blastoporphyritic fabric, the rock becoming compact and massive.
Mineralogical Characteristics. Phenocrysts.	Mainly Diopsidic Augite.	Partial or complete replacement by : (1) Amphibole. (2) Amphibole and biotite. (3) Amphibole, biotite and chlorite. All may contain one or more released minerals.	With increasing removal of material replacement by : (1) Pennine and tremolite. (2) Pennine, ferroantigorite and tremolite. (3) Tremolite, antigorite and talc.	Gradual replacement of chloritic pseudomorphs by tremolite porphyroblasts.
Mineralogical Characteristics. Groundmass.	Mainly Plagioclase and Some Granular Augite.	Replaced by amphibole, with or without chlorite. Small grains of epidote, quartz, calcite and iron ore are also present.	With increasing removal of material, replaced by : (1) Tremolite, pennine and epidote. (2) Ferroantigorite, pennine, tremolite and epidote. (3) Antigorite and tremolite.	Replaced by fine tremolite, followed by the formation of large masses across the earlier formed schistosity
Veins formed by released material.	——	Calcite and epidote form veins and vugh-like areas in groundmass. Also tend to accumulate in areas of least stress.	Released material generally removed.	Released material still removed.

have become converted into elongated flattened lenses but have not been obliterated (Figs. 3A and 4D). In the fine grained groundmass a marked schistosity is always produced at an early stage.

The formation of compact massive rocks in certain areas as a result of the reintroduction of solutions could take place only under conditions of reduced stress. It seems that here the highly cleaved rocks become so saturated with solutions that stress was almost eliminated. In addition, by this time, directional pressure may have diminished throughout the area.

(b) Mineralogical Transformations.

In the Wellington district there was no regional metamorphism prior to faulting ; the original igneous rocks were thus sheared, without suffering previous regional metamorphism. Mineralogical changes produced are of a retrogressive character, but since they are imposed on igneous rocks they must be called dynamic rather than retrogressive changes.

The colour of the rocks ranges from green to purple, depending on the amount of magnetite and hæmatite in the groundmass. This *separation of iron oxide* seems to have taken place prior to faulting, as it is evident even in the least altered types. The release of iron ore as a deuteric process is fairly common in the Silurian andesites of the Wellington district. In the purple schists the amphibole developed as a result of dynamic metamorphism contains very little of the actinolite molecule, and the chlorite is a positive pennine which is practically colourless. This indicates that this iron was not available for the mineralogical reactions resulting from the later dynamic metamorphism, which further suggests its separation prior to metamorphism. In the green schists, which contain only a small amount of magnetite, the amphibole ranges in composition from actinolite to pargasite, and the chlorite is a marked green. Hence a considerable proportion of iron has entered into their composition. Very pleochroic epidote is produced in the latter types, while pale epidote or clinozoisite often occur in the former.

The *type of replacement of the pyroxene* to the east of Poggy Creek is very variable. As already discussed by many authors, the mineralogical changes must involve reaction with other minerals, chiefly plagioclase. In the epidiorites of the South-Western Highlands (Wiseman, 1930) and those from the Start area, South Devon (Tilley, 1938), the amphiboles are actinolitic varieties and the chlorite, aluminous pro-chlorite. The rocks from the east of Poggy Creek, which have not suffered much removal of lime and alumina, contain amphibole ranging from tremolite to actinolite and rarely pargasite. The chlorite in these areas belongs to the pennine group and is therefore a less aluminous variety than that developed in the other localities. The original augite was a diopsidic variety and would contain only small quantities of alumina. Therefore, as in the South-West Highlands and the Start area, it must have been the basic plagioclase which supplied the alumina necessary for the formation of the amphiboles and chlorites. Where the basic felspar had previously been converted into masses of epidote with small quantities of albite, the alumina would be derived from the epidote.

The formation of biotite, together with amphibole, from the pyroxene, may have been due to the presence of small quantities of potash in the original mineral. Biotite is also present in the groundmass of some schists. Here also alumina must be derived from the felspar or epidote. In a schist from the Highlands Wiseman (1934) suggests that potash solutions are brought in during retrograde metamorphism, and they may have been introduced here.

In some of the lowest grade schists needles of amphibole are developed in the plagioclase of the groundmass, while at a more advanced stage the felspar is completely replaced. For this *amphibolisation of the plagioclase* magnesia

must have been introduced unless sufficient chlorite was contained in the original felspar. The source of magnesia, then, could only be the pyroxene, and some of the magnesia which would normally give rise to chlorite must have been utilised in the production of more amphibole. The alumina of the plagioclose is either incorporated in the amphibole or removed to other parts of the rock. In some cases chlorite is practically absent. Occasionally, however, schists in which the felspar has been entirely replaced contain only small quantities of amphibole, but much pennine. Here the alumina is probably derived from the epidote molecule, since large quantities of epidote occur in veins and granular masses. The development of amphibole or chlorite in the altered groundmass probably depends on the relative amounts of magnesia, lime and alumina, and it is likely that even here some migration of material has taken place. However, at times the chlorite may have been produced from the amphibole and biotite.

The conversion of basic plagioclase into albite and epidote is considered by Wiseman (1934) to be rare under conditions of faulting. He cites many cases of crushed basic plagioclase occurring in rocks which otherwise show marked retrograde changes, but he gives a few examples where felspar has been altered. In the low grade types at Wellington, which have only slight directional structures, the felspar is now largely converted into epidote and albite. It is probable that this may be due to crushing in the presence of water. However, the possibility that the alteration was deuteric and pre-faulting cannot be overlooked. Plagioclase as basic as acid andesine occurs in one schist but is clouded (MacGregor, 1931), and is associated with clear, recrystallised grains of albite, so that sometimes, at least, albitisation of the basic plagioclase is the result of dynamic metamorphism.

Accompanying these mineralogical changes there is a *release of material* (lime, alkalies and some alumina and silica). The silica gives rise to quartz in the groundmass and the soda to albite, although both may be locally removed. The lime may be united with varying quantities of iron and alumina to give epidote, or it may form calcite, the carbon dioxide being introduced. Occasionally the carbonates, and less often the epidote, attack and replace the surrounding minerals of the groundmass. Calcite may occur, together with plagioclase, in amygdule-like areas in the groundmass. Some of these represent partially replaced plagioclase phenocrysts. Others, which have a sporadic distribution and are largely composed of calcite, seem to be the result of segregation during metamorphism. At Start, Tilley gives a similar explanation for such structures. Staining tests fail to reveal any dolomite in association with the calcite, so that magnesia has not migrated.

In this part of the area the material which has been set free by mineralogical reactions still remains in the rock mass as epidote, calcite and quartz, and is not entirely removed.

The *rocks in the fault zone to the west of Poggy Creek* have become intensely schistose, and at times highly cleaved, making the movement of solutions through them easy. Under these conditions material released during mineralogical transformations could be transported. The schists in this part of the area which have been least altered chemically are characterised by the presence of amphibole—a tremolite-actinolite variety—pennine, and small quantities of epidote. With further removal of lime less tremolite and epidote occur but the magnesian-iron mineral ferroantigorite is widely developed. Where there has been much separation of iron oxide resulting from deuteric activity, antigorite is produced instead of ferroantigorite, the reason being similar to that already discussed in the case of tremolite (see p. 76). The analyses of the two rocks (Table II, columns II, III) show approximately equal amounts of iron. At a still more advanced stage talc is formed. The relative amounts of lime and alumina removed are variable, for some schists contain tremolite,

antigorite and talc, and others pennine and antigorite. In the former there has been considerable removal of alumina and in the latter, of lime. Here the minerals produced are essentially stress minerals, their development being made possible partly by the abundance of water.

Throughout much of the area there is little indication of the released material in the rocks. In one part, however, veins of calcite occur, while some schists contain granular epidote. Quartz and albite are absent from this part of the region.

Where lime has been reintroduced, much massive tremolite is developed and pennine and antigorite gradually decrease. In the earlier stages the magnesia released by the formation of tremolite from antigorite gives rise to talc, but on further addition of lime it is all used in the production of tremolite. The gradual disappearance of pennine indicates the removal of alumina.

(c) Chemical Evidence for the Migration of Material.

The contact altered felspar-bearing amphibolite, which crops out on the Wuuluman Road crossing of Poggy Creek, is considered to be similar in composition to the unaltered lamprophyre from which the dynamic types were developed. It comes from the least altered portion of the same sill, but directional structures indicate that it suffered some shearing prior to contact metamorphism. An analysis of this rock is given in Table II, column I. Analyses were also made of the pennine-ferroantigorite-tremolite schist (Table II, column II), the antigorite-tremolite-talc schist (Table II, column III) and the tremolite rock (Table II, column IV). It is not possible to compare these

TABLE II.

Analyses of Rocks Collected from the Poggy Creek Sill.

	I.	II.	III.	IV.
SiO_2..	49·24	41·08	45·51	51·31
Al_2O_3	13·85	11·28	7·60	5·13
Fe_2O_3	4·88	2·16	6·40	3·47
FeO	6·55	6·72	2·87	3·58
MgO	8·34	23·25	26·30	22·37
CaO	10·94	7·40	4·25	10·39
Na_2O	2·55	0·55	0·05	0·03
K_2O..	1·32	0·69	0·89	—
H_2O+	0·72	5·03	4·01	2·78
H_2O-	0·16	1·10	1·79	0·25
TiO_2	0·62	0·49	0·23	0·21
P_2O_5	0·31	0·37	0·10	0·05
MnO	0·17	0·15	0·17	0·15
Total	99·65	100·27	100·17	99·72
Sp. Gr.	3·09	2·88	2·84	3·02

I. Felspar-bearing Amphibolite. Wuuluman Road Crossing on Poggy Creek. Anal. E. M. Basnett.

II. Pennine-ferroantigorite-tremolite schist. Por. 48, Par. Nanima. Anal. E. M. Basnett.

III. Antigorite-tremolite-talc schist. Por. 48, Par. Nanima. Anal. E. M. Basnett.

IV. Tremolite rock with a little pennine. Por. 48, Par. Nanima. Anal. E. M. Basnett.

analyses calculated on a volume basis since changes in volume have most likely taken place during dynamic metamorphism. An attempt at comparison has been made by the use of a triangular diagram based on molecular numbers (Fig. 10). Al_2O_3 represents alumina after satisfying Na_2O and K_2O; CaO equals total lime, while (Mg . Fe)O represents total magnesia and the FeO remaining after normative ilmenite and magnetite have been formed. Analyses I, II, III, IV of Table II are represented on the diagram by the points 1, 2, 3, 4 respectively. While it is not considered advisable to lay too much stress on this diagram it would seem to support the evidence given by the mineralogical constitution of the rocks.

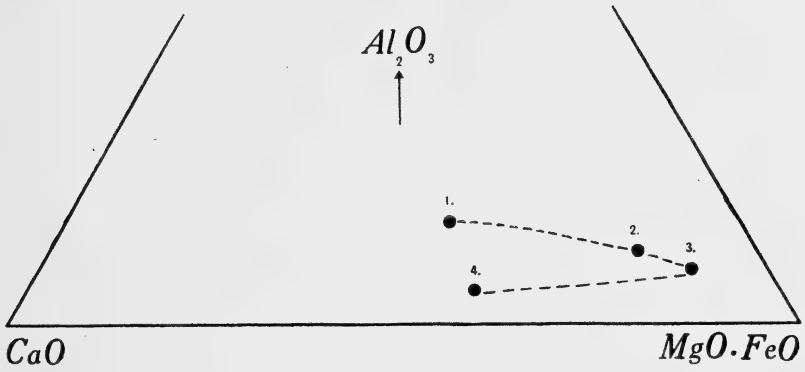

Fig. 10.

Comparing points 1 (felspar-bearing amphibolite) and 2 (pennine-ferro-antigorite-tremolite schist) it is obvious that much lime and a smaller quantity of alumina have been removed. The point 3 (antigorite-tremolite-talc schist) shows the process carried still further. The apparent increase in iron and magnesia in these rocks is due to the removal of the above mentioned constituents and not to an addition of magnesia and iron. This is emphasised by the lack of magnesia-bearing minerals in the veins. Point 4 (the tremolite rock) compared with point III shows a marked increase in lime and a slight decrease in alumina. This is indicated mineralogically by the development of tremolite and the disappearance of pennine. The decrease in magnesia and iron is again only relative and talc is produced in the less altered types.

From an examination of the rocks and their analyses (Nos. I, II, III, Table II) it is concluded that lime, alumina, alkalies and some iron, released in the mineralogical changes, must have been transported by the circulating solutions. The rare occurrence of calcite veins in these rocks and their abundance in the less sheared types to the east of Poggy Creek indicates that most of the lime migrated as the potential calcite molecule. Finely divided epidote in some schists, and veins of this mineral in those to the east of Poggy Creek suggest that some lime and all the alumina was removed as the potential epidote molecule. Although felspar is absent in the zone of intense shearing, it is abundant in the schists to the east of Poggy Creek, so that the removal of soda in this form is probable.

The material which takes an active part in the later mineralogical transformations resulting in the formation of the tremolite rock (Anal. IV, Table II) is probably that released by earlier reactions and stored in the circulating solutions. However, it is chiefly lime and silica which cause these changes, while the alumina is apparently still being removed.

All these mineralogical and chemical changes must have taken place at low temperatures and in the presence of considerable quantities of water and carbon dioxide.

(iii) Contact Metamorphism.

The contact altered lamprophyres have been divided into a felspathic and a non-felspathic group. One of the former (Table I, column III) and two of the latter have been analysed, a spinel-amphibolite (Table I, column I) and an epidote amphibolite (Table I, column II). It is evident that the non-felspathic types have been developed from the more basic lamprophyres. They contain high magnesia and lime and relatively low alumina, but this relation is reversed in the more acid types. This is expressed in the composition of the amphibole. In the non-felspathic types it belongs to the tremolite-actinolite series, one exception being found in the epidote amphibolite, in which it is a negative pargasite. In the most acid varieties the amphiboles are members of the pargasite group. Alumina in the non-felspathic amphibolites is present in epidote, clinozoisite, pennine and occasionally small quantities of mica or pleonaste. The alkalies occur in the mica, but where this mineral is not produced, they must enter into the composition of the amphibole. As before, plagioclase is involved in the formation of the amphibole and pennine.

Some amphibolisation of the pyroxene probably took place prior to the injection of the granite as a result of either deuteric or of dynamic alteration. Since the pyroxene in the least altered types shows no amphibolisation, deuteric activity may be disregarded. The effect of dynamic alteration must have been considerable, as directional structures are still preserved. However, the lamprophyres have been converted into amphibolites throughout the entire contact zone. If the granite were injected before stress had completely subsided, as seems likely since there are signs of strain in some of the aplite veins to the south of the granite, then amphibolisation commenced by dynamic pressure would be continued during contact metamorphism. The development of amphibole in the absence of stress would have obliterated earlier schistose structures, and this has happened in only a few places. However, all specimens show signs of the development of a granoblastic fabric.

The production of spinel in the amphibolite resulted from an original low content of silica and lime as compared with magnesia and iron. The occurrence of diopside in unstable equilibrium in the amphibolites is probably due to a relatively high lime content and higher temperature conditions.

The presence of amphibole and chlorite in certain of these rocks shows that generally the alteration took place under low grade wet conditions. The amphibolisation of the pyroxene is variable, particularly along the southern margin of the granite, and may be due either to difference in temperature, or to the abundance of available water.

(iv) Hybridisation.

The hybridised veins can be traced to aplite veins. The aplite consists essentially of quartz, microcline, oligoclase, and a little biotite. The hybridised veins show important mineralogical differences. Biotite disappears, quartz is rarely present, potash felspar varies in amount, and plagioclase is acid andesine. The ferromagnesian mineral produced from the hybrid magma is diopside. Apatite becomes abundant.

Directional structures in the surrounding rocks could only have been developed by dynamic metamorphism. Signs of strain in the aplite veins indicate that stress was still operating to some extent after their injection. Thus lime and alumina released during the dynamic changes may still have been

in solution. Hence the invading magma may have obtained these constituents either from this source, or from carbonates and epidote already deposited. This increase in lime and alumina would enable a more basic plagioclase to crystallise from the hybrid magma.

The addition of lime, together with higher temperature conditions, must be responsible for the development of diopside in the amphibolised phenocrysts of the lamprophyre adjacent to the vein, and in the vein itself. The magnesia must have been derived largely by reciprocal reaction from the ferromagnesian minerals of the invaded lamprophyre, since the potential biotite molecule of the aplite would have contained insufficient for the development of considerable quantities of diopside. Hornblende, which is present as xenocrysts in the veins, is mainly changed to diopside, and thus appears to be unstable in the invading magma. The production of these new minerals must account for the absence of quartz in many of the hybrid veins.

VI. Summary.

It has been shown that the lamprophyres crop out in a series of parallel sills. After injection the igneous rocks were subjected, first to intense dynamic metamorphism due to local faulting, and later to contact metamorphism resulting from the injection of the Wuuluman granite.

In the area of greatest shearing, material set free during resultant mineralogical changes has been almost entirely removed from the rocks. Where these are less schistose, it accumulates in veins and vugh-like masses. In certain localised areas a reintroduction of material stored up in the circulating solutions has been responsible for the formation of lenses of compact tremolite rocks within the chloritic schists.

The contact altered lamprophyres may be divided into a felspathic and a non-felspathic group. The majority of these rocks have undergone slight dynamic metamorphism prior to contact metamorphism, as directional structures are still visible in some places. It is probable that dynamic pressure had not completely subsided before the intrusion of the granite.

Aplite dykes and stringers of granitic material intrude the lamprophyre along the southern margin of the granite, and mention has been made of the hybrid changes involved.

VI. Acknowledgments.

In conclusion the writer wishes to thank Dr. G. A. Joplin and Dr. W. R. Browne for their kind criticism and helpful suggestions, and also Mr. and Mrs. W. Powell of Willunga for their hospitality and assistance during field work.

References.

Jones, L. J., 1935. Geological Survey of the Wellington Goldfield. *Ann. Rept. Dept. Mines, N.S.W.*, p. 76.

Larsen, E. S., and Berman, H., 1934. The Microscopic Determination of the Non-Opaque Minerals. *U.S. Geol. Surv. Bull.* 848.

MacGregor, A. G., 1931. Clouded Felspar and Thermal Metamorphism. *Min. Mag.*, **22**, No. 133, p. 524.

Matheson, A. J., 1930. The Geology of the Wellington District, N.S.W., with Special Reference to the Origin of the Upper Devonian Series. *Journ. Proc. Roy. Soc. N.S.W.*, **64**, 188.

Tilley, C. E., 1923. The Petrology of the Metamorphosed Rocks of the Start Area (South Devon). *Q.J.G.S.*, **79**, 180.

———— 1938. The Status of Hornblende in Low Grade Metamorphic Zones of Green Schists. *Geol. Mag.*, **75**, 497.

Winchell, N. H., and A. N., 1927. Elements of Optical Mineralogy. New York, Pt. II, p. 373.

Wiseman, J. D. H., 1934. The Central and South-Western Highlands Epidiorites : A Study in Progressive Metamorphism. *Q.J.G.S.*, **90**, Pt. 3, 354.

H—April 1, 1942.

THE TERTIARY LAND SURFACE IN SOUTHERN NEW ENGLAND.

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The region to be discussed in this paper lies between Glen Innes and Tamworth, and comprises the southern portion of the New England Tableland.

Accounts of the physiography of this area have been given by E. C. Andrews (1903, 1904, 1910).

Of particular interest are the basalt-capped hills which are the remnants of great floods of lava which were poured out during Tertiary times. The fact that the outliers are numerous and closely spaced for the most part, suggested to the writer a method for the determination of the configuration of the pre-basalt land surface.

The accompanying map is the outcome of the investigation, and shows possible form lines together with spot heights and the basalt outcrops.

Expenses in connection with the field work involved were covered by a grant from the Commonwealth Research Fund.

Method of Investigation.

Taking as datum the present level of the sea, the configuration of the surface below the basalt was deduced from aneroid readings of the heights of the base of the basalt at many points.

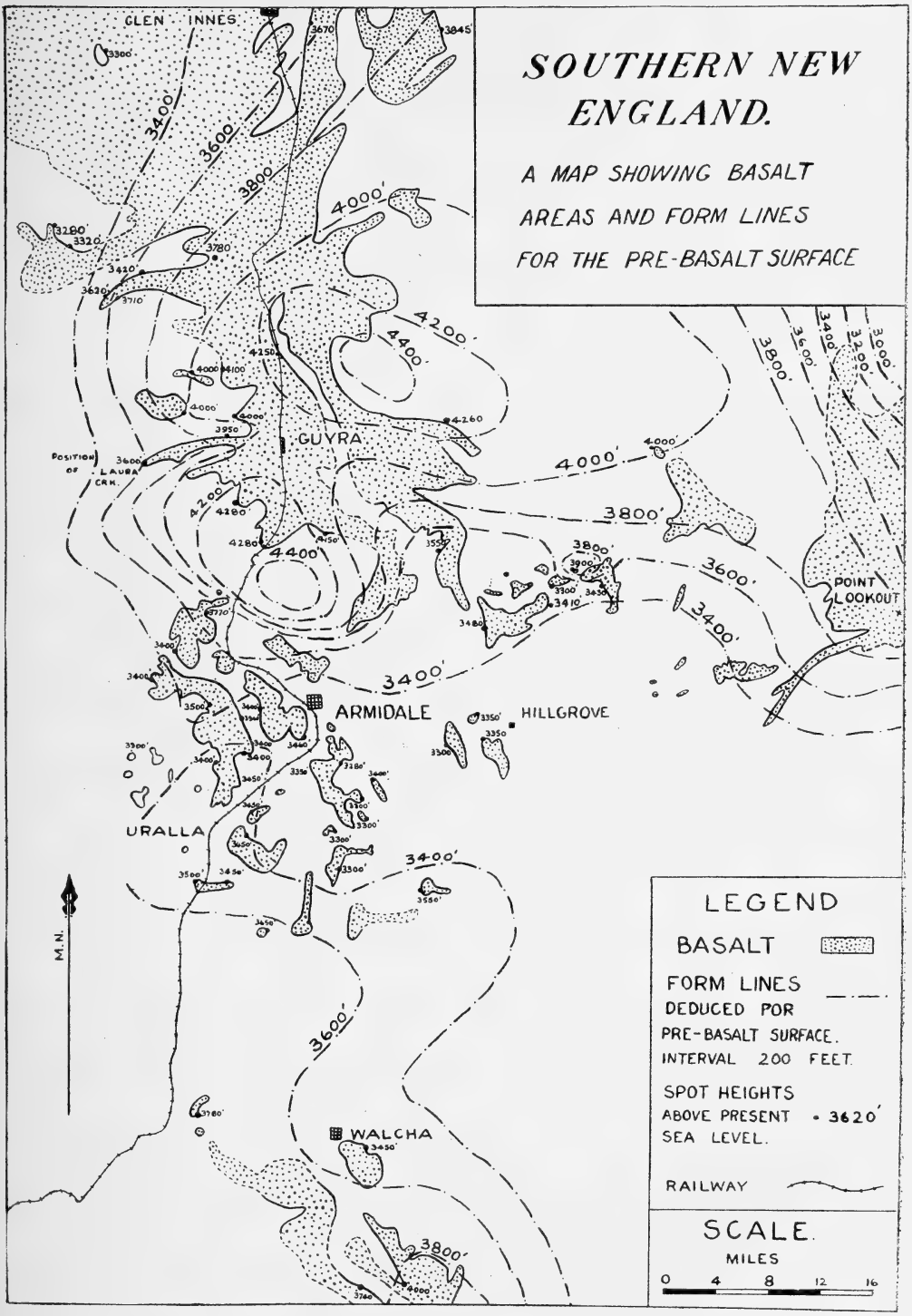
Where the outliers were found to be closely spaced the points obtained on the surface were more numerous than elsewhere and, hence, the information was more complete.

Where large basalt areas were examined it was recognised that the surface beneath this cover could vary considerably in height from point to point. The assumption of a more or less uniform dip corresponding with measurements taken around the margins of the basalt was likely, then, to introduce inaccuracies, but in the absence of information from bores it seemed to be the only possible course to follow.

Between the basalt outliers Tertiary sediments cover quite large areas. The upper layers of the beds have been silicified in places to give rise to the rock known as " grey billy ". This capping remains as a protection against the erosion of the underlying sediments in many regions from which all the basalt has been eroded.

When " grey billy " was encountered it was assumed that it marked the level of the pre-basalt surface.

In places where Tertiary rocks occurred and any possible " grey billy " capping had been eroded, approximate heights were obtained by studying the stratigraphy of the Tertiary beds and estimating the probable thickness of overlying eroded beds. Over much of the area examined erosion has removed both basalt and Tertiary sediments, but in most localities it was possible to hazard a reasonable guess as to the possible previous continuation of them between the present outcrops.


SOUTHERN NEW ENGLAND.
A MAP SHOWING BASALT AREAS AND FORM LINES FOR THE PRE-BASALT SURFACE
GLEN INNES
GUYRA
ARMIDALE
HILLGROVE
URALLA
WALCHA
POINT LOOKOUT
POSITION OF LAURA CRK.
M.N.
LEGEND
BASALT
FORM LINES DEDUCED FOR PRE-BASALT SURFACE. INTERVAL 200 FEET.
SPOT HEIGHTS ABOVE PRESENT SEA LEVEL. • 3620'
RAILWAY
SCALE.
MILES
0 4 8 12 16

Inequalities of the pre-basalt surface are indicated by land rising above the extrapolated heights of the bases of the volcanic rocks in the neighbouring occurrences. A striking example of this is the case of Mount Duval, which rises well above the bases and, indeed, the upper surfaces of the surrounding basalt outliers. How much higher this point and others rose at the time of the volcanic eruptions could not be determined because they have been reduced by erosion since that time. The heights allotted to these points, then, must be regarded as minimum values.

The Pre-Basalt Surface.

It may be seen from the form-line map that the inequalities of the pre-basalt surface amounted to over 1,400 feet (i.e. from 3,200 feet to 4,600 feet with reference to present sea level). That this difference is not to be accounted for by post-basalt movements as suggested by Andrews (1910, P478) is shown by the presence of basalt in valleys eroded out of the highlands. The best example of this observed lies between Baldersleigh and Guyra. The basalt has flowed down the valley of Laura (or Sandy) Creek.

Silicified gravel occurs beneath the flow 400 feet below the upper surface of the granite which forms the walls of the narrow valley. This occurrence proves only a difference of 400 feet in elevation, but the valley filled is juvenile and, hence, its floor is likely to have been a considerable height above the lowest land of the region during Tertiary times.

Mount Duval must have been a prominent feature on the pre-basalt surface. Running north from it, but at a somewhat lower level, was a ridge of land which continued to the vicinity of Glen Innes and probably beyond this point. South of Mount Duval and around the present site of Armidale was a lake into which most of the streams flowed. Beyond the lake the land rose gradually towards Walcha.

It would appear that the Main Divide was approximately in the same position that it is today.

The Tertiary Sediments.

The position of the Armidale lake is marked by the remnants of the sediments which accumulated therein, and its margins are indicated by the change from lake deposits to fossil immature soils. These soils reflect the nature of the underlying rock, and obviously have not been transported by streams. The lake sediments consist of conglomerates, grits and sandstones which are overlain by a thin band of ferruginous cherty shale containing abundant well-preserved plant remains. This shale is a good criterion for the identification of the deposits.

Tertiary rocks south of those formed in the lake are exposed in the parish of Tiverton, and at Uralla. To the north they are well developed in the neighbourhood of Black Mountain. Here, the remains of sticks were seen in the "grey billy". The cherty shales have not been located in this locality and, indeed, it is not to be expected that the lake would have extended into what must have been high country at the time of its existence around Armidale.

The presence of the lake in the lowest portion of the area indicated by the form lines lends confirmation to the view that the inequalities of the surface were due to pre-basaltic erosion and not to later differential uplift.

The Basalts.

The lava flows seem to have been poured out on the higher ground of the Guyra region and to have run down the valleys towards the lower ground. They reached the Armidale lake and buried it to a depth of some hundreds of feet. The total original thickness of basalt in any area is indeterminate owing to the great amount of post-basalt erosion. In places it exceeded a thousand feet

since more than this amount, made up of a number of different flows, still remains at Point Lookout. No attempt to link up individual flows throughout the region has been made so far. There is no evidence to indicate that there were two different outbursts of volcanic activity separated by a long interval of erosion in this region.

It is not proposed to discuss the age of the basalt since the problem is one of Australian interest, and many parts of the continent besides that described above would have to be considered.

Bearing upon the problem is the presence of abundant fossil leaves, including the so-called *Cinnamomum*, and it is proposed to discuss this flora in a subsequent publication.

References.

Andrews, E. C., 1903. An Outline of the Tertiary History of New England. *Rec. Geol. Survey N.S.W.*, vii, Pt. 3.

Andrews, E. C., 1904. The Geology of the New England Plateau. Part 1. *Rec. Geol. Survey N.S.W.*, vii, Pt. 4.

Andrews, E. C., 1910. Geographical Unity of Eastern Australia in Late and Post Tertiary Time. *J. Roy. Soc. N.S.W.*, **44**.

SPERMATORRHŒA IN MARSUPIALS, WITH SPECIAL REFERENCE TO THE ACTION OF SEX HORMONES ON SPERMATOGENESIS OF *TRICHOSURUS VULPECULA*.

By Adolph Bolliger

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Manuscript received, April 14, 1942. Read, May 5, 1942.

Since the observation was made some three years ago[1] that the urine of some male marsupials, e.g. *Trichosurus vulpecula*, *Perameles nasuta*, *Caloprymnys campestris*, contained spermatozoa, over a thousand urine specimens from forty male possums or phalangers (*Trichosurus vulpecula*) and from other marsupials have been examined under normal and experimental conditions. After some remarks on the method of collecting and examining urine specimens, these findings will be described under the following headings:

(1) Spermatorrhœa and spermatozoal motility in normal fully grown phalangers and other marsupials.

(2) The action of gonadotropic hormone on spermatogenesis.

(3) The action of œstrogens on spermatogenesis.

(4) The action of testosterone on spermatogenesis and spermatozoal motility.

(5) The action of progesterone on spermatogenesis.

Method of Collecting and Examining Specimens.

In most instances the vestigial cloaca present in marsupials does not interfere with the collection of urine free of fæces. As pointed out before, urine can be obtained by pressing on the lower part of the abdomen or by placing the animal in a metabolism cage.[1] For *Trichosurus vulpecula* the quickest and most effective method is to have the animal held by an assistant and to grasp the bladder through the abdominal wall. Provided it contains some urine, the bladder is easily located and pressure on it initiates urination. The urine is best collected in a centrifuge tube. Sometimes it is advisable to collect the urine in two or more consecutive tubes because the first few millilitres voided may contain large amounts of phosphate and carbonate which may hide many of the spermatozoa from view. If it is only a question of numbers of spermatozoa present, phosphates and carbonates can be dissolved by adding a trace of acetic acid (20%). In a urine treated in this manner the spermatozoa can be counted in a counting chamber for blood-cells, there being usually no other obstructing materials present except a few so-called prostatic bodies. In the present investigation, however, counting was rarely done and in the first instance the urine was examined for the presence or absence of spermatozoa. For this purpose a drop of the uncentrifuged urine was examined microscopically and the urine was considered to contain a normal amount of spermatozoa if more than five spermatozoa were found to be present in a low power microscopic field. In a urine of average concentration anything below five was considered as probably abnormal and a fresh specimen obtained a few hours later was examined to verify this impression.

The spermatozoa were also examined for motility in fresh unacidified urine kept in a stoppered vessel at room temperature and at 38° C.

The differences in motility have been recorded as :

(*a*) Strongly motile.
(*b*) Motile.
(*c*) Vibrating.

(*a*) Strongly motile spermatozoa moved rapidly across the field of the microscope.

(*b*) Motile spermatozoa showed intense movement of the body and the tail but swam about the field only sluggishly or not at all. Strong motility and motility could be readily observed under low power magnification (×70 approximately).

(*c*) Motility of a vibrating nature could only be seen distinctly under higher power magnification (×370 approximately). This was usually a rapid oscillating movement sometimes more pronounced in the head and body and sometimes more pronounced in the tail of a stationary spermatozoon.

(1) Spermatorrhœa in Normal Fully-grown Phalangers.

On examining the urine of adolescent male possums (*Trichosurus vulpecula*) kept in captivity, it was noted that spermatozoa began to appear in it only when the animal, judging by its bodyweight and its appearance, such as size of testicles, was fully grown. This was at an age of more than one year, and usually less than two years. For the first few weeks spermatorrhœa was somewhat irregular, i.e. a few spermatozoa were present in one specimen and absent in the next one. But after this initial period, spermatozoa in large amounts were found in any specimen of urine measuring 1 ml. or more, obtained at any time of the day or any time of the year. In the great majority of cases they numbered about from 10-100 in any low power field examined under a microscope, the number depending to a certain extent, on the dilution of the urine and as to whether the specimen was obtained from a very full or only slightly filled bladder. In the case of a full bladder, spermatozoa were much more numerous in the first 10 ml. than in the last 10 ml. out of the total volume of about 50 ml. Most of the spermatozoa voided with the urine were usually of normal appearance. When viewed on the flat they exhibited the characteristic arrow or spade-like head (Fig. 1). Identical findings were obtained from a kangaroo rat (*Æpyprymnus rufescens*) observed for a period of one year.

Spermatozoal Motility.—Originally it was stated that the majority of spermatozoa obtained in the urine are non-motile and that only a very few may be still moving about in a sluggish fashion.[1] However, after studying the spermatozoa carefully under high power magnification (×370 approximately) it was noted in addition to the rare motility observed under low power magnification that in the majority of specimens many more and sometimes as many as half of the spermatozoa present showed a form of motility which has been designated as " vibration ". These spermatozoa were stationary, but their bodies showed fast vibrating movements which sometimes were pronounced in only a part of the spermatozoon, such as the region of the head or the tail. If the urine was kept in a stoppered vessel these oscillations persisted for about 1 to 4 hours at room temperature. Cooling the urine down to 4° C. and warming it up again to 38° C. did not materially influence longevity.

Finally " strong motility " and widespread " motility " were also observed when a special attempt was made to study spermatorrhœa during the main breeding period in autumn. On fine days following a week of rain late in March, 1942, it was observed that all the five male possums kept in the laboratory exhibited widespread spermatozoal motility. Varying numbers of spermatozoa

exhibited strong motility, i.e. they moved about at great speed in the drop of urine examined. The longevity of these spermatozoa in urine was remarkable because in some instances motility was still observed nine hours after voiding the urine.

Fig. 1. Spermatozoon and some débris from fresh urine of *Trichosurus vulpecula*, unstained. Magnification ×1,000 approx.

This qualitatively and quantitatively increased motility persisted for about 1-2 weeks. During this period the possums in the laboratory mated and those obtained from the bush were pregnant, as evidenced by the appearance of pouch young in the following week.

In this connexion it may also be mentioned that males may be fertile at least twice or probably several times during the year. For example, it was observed in our laboratories that one male sired two successive young in the same female in the same year. Furthermore, pregnancies were observed which did not refer to the general breeding seasons in autumn and spring. This would indicate that at least some males must be capable of producing fertilisation in between breeding seasons.

Phalangers and other marsupials possess comparatively large testicles which on histological examination appear to be producing large numbers of spermatozoa throughout the year. A great number of them can be stored in the epididymis but only few in the vas deferens, which in *Trichosurus vulpecula* and other marsupials is a narrow tube without an ampulla. There is, however, a definite enlargement in the lumen of the prostatic urethra beginning only a few mm. below the bladder neck at the point where the vas deferens enters the prostatic urethra and extending through the greater part of this organ.[2] On examining the contents of this enlarged section of the urethra numerous spermatozoa were found to be present, and it may be quite probable that spermatozoa emerging in a more or less even flow from the vasa deferentia are stored in this widening and are flushed out on micturition. However, even the bladder may under certain conditions act as a storehouse for spermatozoa, since they were always found in considerable amounts in the urine contained in this organ in animals which had been killed. The entry of spermatozoa into

the bladder could be explained by the very close position of the openings of the vasa deferentia in relation to the bladder opening. In addition to this flushing out effect, it is also quite probable that on micturition larger numbers of spermatozoa are expelled from the vasa deferentia into the uro-genital canal, where they would mix with the urine coming from the bladder.

(2) The Action of Gonadotropic Hormone on Spermatogenesis.

Two immature male possums of six and ten months of age respectively were given 4 injections of 250 international units of chorionic gonadotropic hormone obtained from human pregnancy urine (Gonan B.D.H.) over a period of three weeks. The younger animal (bodyweight 0·73 kg.) being too immature, showed no definite response and did not develop spermatorrhœa within the next four months.

The older animal (body weight 1·5 kg.) was still a typically immature specimen as indicated by its bodyweight, size of testes and general appearance. The testicles were about the size of a large pea (approximate diameter 0·7 cm.) and the urine contained no spermatozoa. Six weeks after beginning the injections a few spermatozoa were observed in the urine. At this stage the animal was still typically immature in appearance (body weight 1·6 kg.) but the scrotum was elongated and its vessels engorged. The testes were very firm and had increased in size (diam. 1·1 cm.). During the next fortnight approximately 1-6 spermatozoa were observed per low power microscopic field, and a few specimens contained none, but after this spermatorrhœa became as marked and as consistent as in fully grown animals. Increased numbers of them were motile and many vibrating. Simultaneously the animal showed rapid general development, and two months after beginning the injections it was found to weigh 2·4 kg. Controls of similar age did not exhibit spermatorrhœa at any stage of the experiment. Therefore it was concluded that gonadotropic hormone brought on precocious spermatorrhœa.

Similar amounts of gonadotropic hormone were injected into fully grown animals. No definite response was noted, but it was felt that the number of spermatozoa had increased on account of the injections.

(3) The Action of Œstrogens on Spermatogenesis.

On previous occasions it has been shown that œstrogens, natural[2] (œstrone, œstradiol esters) or synthetic[3] (stilbœstrol, hexœstrol) inhibit spermatogenesis. However, to bring on this result large doses are required which seriously interfere with the general health of the animal and frequently lead to its death. For example, the weekly injection of 0·5 mgm. of stilbœstrol over a period of 5 weeks (total amount injected 2·5 mgms.) did not diminish spermatorrhœa while the total injection of 7 mgms. administered over a period of 3 weeks led to complete suppression of spermatorrhœa. This animal, however, died from the toxic effects of the stilbœstrol and on microscopic examination of testes no spermatozoa were seen. A further experiment (S51) where 4·5 mgms. were given over a period of 3 weeks resulted in only a temporary loss of spermatogenesis. This and another experiment (H50), although mentioned in a previous paper[4] will be described individually because they represent features not yet sufficiently emphasised.

Experiment S51.—The course of this experiment has been described for a period of seven months. The injection of stilbœstrol (1·5 mgm. per week for three weeks) brought on testicular ascent. However, in the sixth month of the experiment the external signs of the action of the hormone such as loss of weight and scrotal and testicular atrophy had mostly disappeared and spermatozoa were produced as evidenced by spermatorrhœa. At first they were not numerous and frequently they appeared to be deformed. Within a week, however, they

were as numerous as in controls, but in contrast to the controls, motility and markedly increased vibration were observed. To test the fertility of the animal it was mated with a female which shortly afterwards was found to be pregnant.

Experiment H50.—This animal received injections of 2 mgm. of hexœstrol twice a week over a period of four weeks. Spermatorrhœa was present before the injections were begun and persisted during the first two weeks. For a period of three months after this no spermatozoa were observed in the urine; then spermatozoa began to reappear in the urine, though in small numbers and frequently abnormal in size and shape. Within a fortnight after their reappearance, however, the spermatozoa present in the urine were of approximately normal number and appearance. With regard to motility it was observed in some specimens that for a period of about three weeks, actively motile spermatozoa were present, as well as an exceptionally large number of vibrating spermatozoa in comparison with controls. This temporarily increased, motility subsided again, but spermatorrhœa remained a constant feature as long as the animal was observed, which was a period of 12 months.

These experiments demonstrated that the restoration of spermatogenesis after its inhibition by œstrogens was a permanent one. After the re-establishment of spermatorrhœa, fertility was not interfered with and a temporarily increased motility of the spermatozoa might even indicate increased activity of the gonads.

(4) The Action of Testosterone Propionate on Spermatogenesis and Spermatozoal Motility.

As pointed out before[4] testosterone propionate, when given in large doses over a period of several weeks, may diminish or abolish spermatorrhœa.

However, when only two or three weekly injections of 4-8 mgms. of testosterone propionate had been given, increased motility of the spermatozoa was frequently noted. These findings were made in between breeding seasons on a group of five males and increased vibration lasting for several hours was present in the majority of the urine specimens examined. Many samples showed motility which, in some cases, was observed in practically every spermatozoon. A small number of specimens showed strong motility, i.e. both at room temperature and 38° C. many of the spermatozoa moved about at great speed in the drop examined. In a few cases this strong motility was observed for hours and in one case motility was still observed ten hours after voiding the urine. Generally, in these urine specimens, the spermatozoa behaved as they did during a breeding period described in an earlier part of this paper.

However, as already pointed out the majority of specimens examined after the administration of testosterone propionate, showed only increased vibration or no increase in spermatozoal activity at all. Notwithstanding this fact it was concluded that the markedly increased motility, although only sporadic, was due to the administration of testosterone propionate.

(5) The Action of Progesterone on Spermatogenesis.

On a previous occasion[5] it has been reported that progesterone produces a typically androgenic reaction on the adolescent but almost mature male phalanger. After the weekly injection of 2 mg. of progesterone over a period exceeding two months the penis of these animals was found to be of increased size and protruding from the cloaca for a distance of 3 to 4 cm., while in controls of similar age the copulatory organ is hidden retracted in a preputial fold within the cloacal hillock. As soon as this precocious behaviour was noted in the treated animals, their urine was searched for spermatozoa but with negative results. However, spermatozoa began to appear in the urine at about the same time as they did in untreated controls of similar age; viz. about three months

after the onset of the penial protrusion and as in the untreated animals most of the spermatozoa were not motile. The injections of progesterone were kept up for a period of six months and at frequent intervals the urine was examined. Spermatozoa were always found to be present in approximately the usual amount and predominantly in a non-motile state as in controls. Finally the animals were killed and at post-mortem examination the prostate was found to be about 50% larger than in normal controls.

Discussion.

In the order Marsupialia it has been established for at least two species of its sub-order Diprotodontia, e.g. *Trichosurus vulpecula* and *Æpyprymnus rufescens*, that spermatozoa are excreted in the urine throughout the year. Many of these still show signs of life though suspended in normal urine, and they can be obtained very easily in any amount without ill effects on the donor. This constant voiding of spermatozoa is in marked contrast to the short period of ejaculation of spermatozoa in higher mammals where those spermatozoa which are not ejaculated disintegrate and are ultimately reabsorbed. On the other hand, the release of spermatozoa as observed in the marsupial relates to non-mammals such as reptiles, where the testes discharge their products to a part of the original kidney. The original kidney duct (Wolffian duct) is employed as a vas deferens. In reptiles, therefore, spermatozoa are transported in the urinary flow and must arrive in the cloaca mixed with urine.

In marsupials the vasa deferentia connecting with the extraabdominally situated testicles link up with the urinary tract below the bladder as in higher mammals. Nevertheless the spermatozoa, with a possible exception of the short period of copulation, still depend on the urine as a medium of transport and excretion as in reptiles. It is not known yet how spermatozoa are transported during the act of copulation.

The study of the action of sex hormones on spermatorrhœa of *Trichosurus vulpecula* supports the contention that spermatorrhœa gives a true picture of the state of spermatogenesis of the animal examined, because these findings are essentially similar to those reported on spermatogenesis in non-marsupials, where usually the testes have been examined histologically in order to investigate the production of spermatozoa.

For example, after the injection of chorionic gonadotropin in adolescent *Trichosurus vulpecula*, spermatozoa were observed about three months earlier than they appeared in controls. This undoubtedly was due to precocious spermatogenesis which also has been reported to occur after the administration of gonadotropic substances, e.g. in certain lizards[6] as well as in ground squirrel.[7]

The atrophic actions of large doses of œstrogen on the testes are well recognised, and in rodents the cessation of spermatogenesis has been reported after their administration. This has been confirmed in numerous experiments on possums.[2][3] The outstanding finding in the present report is the observation that complete recovery of spermatogenesis together with proven fertility occurs within one month after the reappearance of spermatorrhœa. The temporary increased motility observed shortly after recovery of spermatogenesis is noteworthy and in view of the findings after the administration of testosterone, one might assume a late androgenic manifestation of œstrogens.

Repeated injections of testosterone propionate impair the function of the testes as pointed out by Moore and Price,[8] as is the case with œstrogens. In our marsupial, *Trichosurus vulpecula*, spermatorrhœa sometimes ceased after the repeated injection of large doses of testosterone propionate, doses which in no way affected the general health of the animal.

The increased motility observed after a few testosterone injections, though marked, was only sporadic. This was interpreted to mean that testosterone

represents only one factor in several necessary to maintain motility and that on comparatively rare occasions all the factors, as for example the correct concentration of the hormone, the correct pH, the optimum amount of prostatic secretion, etc., are present to bring on and maintain the strong motility. The question as to whether such motile spermatozoa suspended in urine as well as lesser motile ones may be fertile, could only be solved by experiments with artificial insemination. Such experiments, however, have not yet been performed.

Summary.

1. In fully grown healthy male marsupials such as *Trichosurus vulpecula* and *Æpyprymnus rufescens*, spermatorrhœa is constantly found throughout the year and is directly related to spermatogenesis. Usually the majority of the spermatozoa voided in the urine are non-motile, but a large percentage of them, though stationary, may show a fine vibratory movement under high power magnification. Actual motility visible under low power magnification is rarely seen except during breeding season, when strong motility is also observed. In such urine specimens a number of spermatozoa remained motile "in vitro" for more than nine hours.

2. Gonadotropic hormone obtained from pregnancy urine when administered to immature animals hastens spermatogenesis.

3. Large doses of œstrogen abolish spermatogenesis as shown by the loss of spermatorrhœa and absence of spermatozoa in the testes. If the animal survives the ill effects due to the administration of œstrogen, spermatogenesis, as well as fertility, are re-established in about 3-5 months.

4. The injection of male sex hormone may confer widespread and sometimes even strong motility on the spermatozoa voided in the urine. The injection of frequently repeated doses of testosterone may diminish or even abolish spermatogenesis.

5. Progesterone does not seem to have any effect on spermatogenesis.

6. These findings have been discussed in brief and marsupial and reptilian spermatorrhœa have been compared.

Acknowledgment.

The author wishes to thank Mr. T. M. Harkness, of Ciba Ltd., for a generous supply of testosterone propionate (Perandren) and œstradioldipropionate (Ovocyclin).

References.

(1) Bolliger, A., and Carrodus, A., 1938. *Med. J. Aust.*, 1118.
(2) Carrodus, A., and Bolliger, A., 1939. *Med. J. Aust.*, 633.
(3) Bolliger, A., and Canny, A. J., 1941. This Journal, **75**, 21.
(4) Bolliger, A., and Carrodus, A., 1940. *Med. J. Aust.*, 368.
(5) Bolliger, A., and Carrodus, A., 1939. *Nature*, **144**, 671.
(6) Evans, L. T., 1935. *Anat. Rec.*, **62**, 213.
(7) Wells, M. J., and Moore, C. R., 1936. *Anat. Rec.*, **66**, 181.
(8) Moore, C. R., and Price, D., 1938. *Anat. Rec.*, **71**, 59.

THE OCCURRENCE OF TWO PHYSIOLOGICAL FORMS OF *LEPTOSPERMUM CITRATUM* (CHALLINOR, CHEEL AND PENFOLD) AS DETERMINED BY CHEMICAL ANALYSIS OF THE ESSENTIAL OILS.

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Leptospermum citratum was described as a distinct species and the chemical composition of the essential oil revealed by Challinor, Cheel and Penfold in 1918.[1] Since that date experimental plots have been established in various parts of New South Wales and Queensland, as well as in Kenya Colony, South Africa, and in the Netherlands East Indies. The essential oils from a number of these plots have been examined, and without exception the results confirmed the chemical composition of the original oils examined in 1918.[2]

The oil from the type species, which consists principally of the aldehydes citral and citronellal, has been an article of commerce for several years past. The war has been responsible for an unprecedented demand, with the result that the price rose to £10 per gallon at the stills in September, 1941. The principal localities for the supply of the oil have been Punchbowl, Whiteville, Baryulgil and Copmanhurst, all in the Grafton district of northern New South Wales.

The tree grows in rocky ledges in inaccessible parts of the Dividing Range, and is very sparsely distributed. The increasing demand for the oil has caused an intensive search for new areas. The essential oils distilled from material collected from these new areas were found to differ markedly in chemical composition from the type species. Field investigations revealed the occurrence of at least two forms growing at Tyndale on Woodford Island, situated a few miles west of Maclean on the Clarence River of New South Wales. One form was observed at Copmanhurst.

Botanically the two forms are identical with each other and the type species. Specimens of each were submitted to Mr. R. H. Anderson, Chief Botanist of the Botanic Gardens, Sydney, who confirmed our own determinations. He did, however, comment on the fact that the characteristic odour of the type species could not be detected in the forms.

The description given in the original paper[1] fits the forms exactly, although flowers of the latter have not yet been seen.

In order to distinguish the two forms, they have been designated variety A and B respectively. The leaves of variety A when crushed between the fingers emit a terpene-like odour resembling γ-terpinene, whilst the foliage of variety B gives a rose-like odour characteristic of geraniol.

The chemistry of the essential oils has not yet been completely elucidated, and further work has been deferred owing to the war.

The purpose of this note is to place on record the occurrence of the two forms, together with sufficient chemical data to enable them to be readily

TABLE 1.

Essential Oils of Leptospermum citratum, *Varieties "A" and "B".*

Date.	Locality.	Yield of Oil.	$d\frac{15°}{15°}$	$a_D^{20°}$	$n_D^{20°}$	Solubility in Alcohol.	Ester No.	Ester No. after Acetylation.	Citral Content.	Remarks.
16/4/1941	Woodford Is., N.S.W.	1·0%	0·8841	+1·68°	1·4760	1·4 vol., 70%			16%	Leaves supplied by C. Savidge, Var. "B".
,,	,, ,,	1·2%	0·8634	+2·35°	1·4795	Insol 10 vol., 80%			—	Leaves supplied by C. Savidge, Var. "A".
25/9/1941	,, ,,	1·3%	0·862	+2·08°	1·4789	Insol. 10 vol., 80%	8·3		—	Collected by authors, Var. "A".
,,	,, ,,	1·0%	0·881	+1·75°	1·4780	1·8 vol., 70%			20%	Collected by authors, Var. "B".
				Samples of Oil Furnished by Distillers.						
4/10/1940	Copmanhurst.	—	0·8764	−1·25°	1·4760	10·0 vol., 80%	3·9	43·7	—	Furnished by J. Pocock, Var. "A".
29/9/1941	,,	—	0·876	+1·47°	1·4753	6·3 vol., 80%	3·2	5·7	—	Furnished by J. Pocock, Var. "A".
,,	,,	—	0·864	+2·63°	1·4790	9·7 vol., 80%	8·9	51·3	—	Furnished by C. Savidge, Var. "A".
				Leptospermum citratum *Type—for comparison.*						
		1·0% to 1·5%	0·8792 to 0·8856	+3·6° to +5·0°	1·4688 to 1·4757	1·0–1·2 vol., 70%			45–50%	Also contains citronellal 35%. Total aldehyde, 75–85%.

identified and separated from the type species. The accompanying table gives the chemical and physical characters of the essential oils distilled from material collected by ourselves in September, 1941, together with those of samples supplied by distillers. For comparative purposes the chemical and physical characters of *L. citratum* type are also included in the table.

The constituents which have so far been identified are as follows :

Variety A.—γ-terpinene b.pt. 179-181° C. (762 mm.), ($d_{15}^{15°}$ 0·851, $a_{20°}^{D}$ +0·24°, $n_{20°}^{D}$ 1·4781 ; m.p. of the erythritol, 235-236°), d-a-pinene (pinonic acid, m.p. 69-70°), cymene (p-hydroxy-isopropylbenzoic acid, m.p. 155-156°), cineol, unidentified terpenes, linalool (?), with small quantities of sesquiterpenes and eugenol, 0·6% (benzoate m.p. 69-70°).

Variety B.—Citral 16% to 20% ($d_{15}^{15°}$ 0·8928, $n_{20°}^{D}$ 1·4883, semicarbazones m.p. 163-164° and 135-136°), geraniol, free and combined as formate and acetate, ($d_{15}^{15°}$ 0·880, $a_{20°}^{D}$ +1·44°, $n_{20°}^{D}$ 1·4699, silver salt of phthalic acid ester m.p. 133°, diphenylurethane m.p. 82-83°), with citronellol and similar esters.

Acknowledgments.

Our thanks are tendered to Mr. C. Savidge, Copmanhurst, and Mr. J. Pocock, Punchbowl, for samples of oil and consignments of foliage and for the valuable assistance during our visit to Copmanhurst in September, 1941, and also to the Forestry Commission of New South Wales, and its officers at South Grafton, for valuable cooperation in this investigation.

References.

(1) Challinor, R. W., Cheel, E., and Penfold, A. R., 1918. *J. Proc. Roy. Soc. N.S.W.*, **52**, 175.

(2) Penfold, A. R., and Morrison, F. R., 1918. Syd. Tech. Mus. Bull. 14, part II, Australian Tea Trees of Economic Value.

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CONTENTS

VOLUME LXXVI

Part II

Page.

ART. VIII.—Clarke Memorial Lecture. The Heroic Period of Geological Work in Australia. By E. C. Andrews, B.A., F.G.S. (Issued November 6, 1942) 96

ART. IX.—The Chemistry of Bivalent and Trivalent Rhodium. Part IV. Polynuclear Complexes of Rhodium and Tin with Tertiary Arsines. By F. P. Dwyer, M.Sc., and R. S. Nyholm, B.Sc. (Issued November 6, 1942) 129

06.174

Journal and Proceedings of the Royal Society of New South Wales

VOLUME LXXVI

PART II

THE HEROIC PERIOD OF GEOLOGICAL WORK IN AUSTRALIA.*

By E. C. Andrews, B.A., F.G.S.

Contents.

Page

Part I. The Great Explorers 96

(i) The geological work of the pioneers not recognised sufficiently—Geology and Geography obviously interlock, however, and early geological progress in Australia was " part of the history of topographical discovery ".

(ii) The difficulties under which the explorers laboured :

(*a*) Topographic, climatic, transport, commissariat, and aborigines.

(*b*) The contemporary backwardness of geological science.

(iii) Their valuable contributions to geology. Example, Charles Sturt.

Part II. State Geological Surveys and the Australian Universities 105

Discoveries of valuable minerals assisted materially in drawing the attention of State Governments to the mining and cultural requirements of Australia.

The foundation of State Geological Surveys—

New South Wales (1850–1854, 1873–).
Victoria (1851–1869, 1871–1878, 1878–).
Queensland (1868–1872, 1875–1879, 1879–).
Western Australia (1847–1851, 1870–1872, 1882–1885, 1887–).
South Australia (1882–).
Tasmania (1899–).

Commencement of lectures at Universities—

Sydney, 1852.
Melbourne, 1855.
Adelaide, 1876.
Tasmania, 1892.
Queensland, 1911.
Western Australia, 1913.

Part III. Some Geological Pioneers hitherto Inadequately Recognised 111

Péron, Stokes, Howchin, Dunn, Carne, Maitland, Gregory, J. W.

Part IV. Some Major Problems in Australian Geology 114

1. The Permian Problem.
2. Glaciation in Australia.
3. Physiographic Problems.
4. The Building of Australia.

Part I. The Great Explorers.

It is contrary to the usually accepted ideas of justice and fitness that the romance of our early geological gropings in Australia should be neglected by us—the heirs to all that picturesque past—for the history of geological progress in Australia is bound up with a wealth of heroic deeds ; with herculean struggles with Nature when in unbending and savage mood ; it is a record of triumphs won in the teeth, as it were, of grim and armed antagonisms. From the year 1797, when Surgeon Bass observed the coal seams in the steep coastal escarpments north and south of Sydney ; when he observed fragments of coal in the stream

* Clarke Memorial Lecture delivered to the Royal Society of New South Wales, May 21, 1942.

gravels of the great ravines dissecting the Blue Mountains and explained their occurrence as due to the denudation of a series of persistent coal seams underlying the whole of the Greater Sydney District, students have attempted to piece together the fragments of the fascinating but complicated story of Australian geological stratigraphy and structure.

Sturt, long ago, set himself the alluring but difficult task of explaining the geological setting of the Sydney District.

At the present time, with the advance which has taken place both in geographical and geological knowledge, together with the greatly increased facilities for subsistence and transport in Australia, there is a tendency among the younger geographers and geologists to look askance at the reports and the maps of the pioneers. To them these appear to be mere crude and hopelessly incomplete attempts as compared with the products of recent and modern work. It is, of course, not to be denied that most of the work accomplished by the pioneers has been done again with greater accuracy, but any neglect of the efforts of the early explorers, such as the curt dismissal of their work as though it were unworthy of serious thought, is a matter for definite regret, for, as will be seen, these pioneers of Australian geography and geology were real heroes, and even the plain unvarnished recital of their epic struggles is redolent of romance, romance which imparts life, pathos, grace, dignity, and grandeur to Australian history.

Australia, in 1788, was a vast unknown area, and the earlier geological work necessarily resolved itself mainly into ascertaining the main features of the general topography and geography. In order thus to evaluate the work of the earlier explorers, it is necessary to consider the topographical, commissariat, and transport difficulties which had to be imagined, and provided for, in a great unknown land, together with the state of geological knowledge at the time that they made their adventurous essays. These points may be considered here in order.

(i) Geographical Difficulties.

The pioneer investigators, first and foremost, were explorers whose main objectives were the discovery of topographical and climatic conditions, suitability for settlement, and, most of all, the safe conduct of their parties back to civilisation. Nevertheless, even when taxed to the utmost to keep body and soul together, they continued to make faithful entries in their diaries concerning the topography, climate, rocks, soils, botany, pasturage, suitability for settlement, and so on, of the country traversed by them. The actual dangers and disappointments to which they were subjected appear not to be well known generally. Suffice it to say that so appalling were the obstacles encountered that only brave men, imbued with a profound belief in their mission, could have faced them to the bitter end. One naturally asks: Who, in all this galaxy of heroic souls, this band, "faithful to the end", is to be acclaimed "brightest and best"? Or, again, who of all those, seeking to elucidate the mysteries of their new continental home, was forced to plumb the most profound depths of misery, anguish, agony, horror and despair?

Was it perchance the intrepid Bass, the hero of the daring voyage of 600 miles, from Sydney to Western Port, in an open whaleboat; who, later, according to report, was made prisoner at sea and condemned to the unspeakable horrors of a living death in the metal mines of South America?

Was it Flinders—joint hero with Bass in the daring venture of 1795 in the *Tom Thumb*, a mere eight-foot cockle shell—when, with the end in sight, as it were, of his grand survey of the whole sweep of the Australian coast, he was called on to endure the sting of unexpected defeat occasioned, according to report, by "shipwreck, tragic suffering, and diabolical treachery"?

Was it the indomitable Eyre, in 1840–1841, when—in his desperate search for water in that area of unspeakable desolation, the shore of the Great Australian Bight—with a mere sponge only, he laboriously gathered the priceless fluid drop by drop from the herbage and stunted vegetation ; or, at a later stage, when he came on the body of the murdered Baxter, and sensed the utter loneliness, destitution, danger, and horror of his position, with his only white companion and friend gone, and he himself deprived of food, weapons, and means of transport ?

Was it the " great and gentle " Sturt, that prince among Australian explorers unable—after his descent of the Murrumbidgee and the Murray—to force a passage through the coastal breakers beyond Lake Alexandrina, and driven to face the heart-breaking return upstream with a crew ill and disabled, and with hordes of hostile savages dogging his path seeking opportunity to ambush and destroy him ? Was it Sturt again, in 1845, facing the horrors of a record drought at Rocky Glen, far to the north of Broken Hill, where he saw the one and only waterhole of the district drying up, but dared not leave it because of the certain death by thirst awaiting him outside ; where the beefwood tree by the camp marking the site of the grave of Poole, his second in command, was a continual reminder of his desperate plight ; where also a little later he was to despair of the life of his friend Harris Browne ; where the average maximum temperature for December, January and February had been 101, 104 and 101 degrees Fahrenheit respectively ; where the screws of all the boxes had been withdrawn by the heat ; the combs and the horn handles of the instruments split into fine strips ; the lead fallen from the pencils ; the fingernails become brittle as glass ; where the wool on the sheep and the hair on the men's heads had ceased to grow ; where, around his imprisoned party, extended the interminable lines of sand ridges ; where, later also, he was called on to choose between the abandonment of his cherished quest for the continental centre or to condemn his party to certain death in the desert ? Was it Sturt at that stage, or later still, when—with his body racked in the unspeakable agonies of scurvy in its acutest form—placed by Harris Browne in a waggon rut to ease his torture somewhat, he had called his faithful servant, Davenport, to him and extracted from him the promise that, in the event of his death, at all costs, he would ensure the safe transmittal to Queen Victoria of a cherished copper specimen found by him during the trip, and which would assure the Home Government of the existence of mineral deposits of value in Australia ?

Was it Kennedy, in 1848, when, dogged by disaster from the start near Hinchinbrook Island, in the form of unceasing rains, interminable pestilential swamps, flooded rivers, interlacing and thorny jungle growths, insect plagues, and murderous blacks, and seeing his one-time large party perishing around him, he had set out for aid, attended by his faithful aboriginal servant Jacky, only to fall exhausted in the jungle, a martyr to starvation, illness, and the spears of aborigines, just as he had come within sight of safety ?

Was it the impetuous Burke, in 1861, when, after the dash across the continent, and finding the depôt on Cooper Creek deserted, he had sunk exhausted in his tracks in a vain attempt to reach Mt. Hopeless, and, feeling his end approaching, had begged his associate, the young soldier, the faithful King, not to leave him before the bitter and imminent end ?

Was it Wills, the amiable high-souled Wills, when, at the limit of his endurance, he had bidden his companions to leave him to his fate and save themselves ; he who had been left to die in utter loneliness, his body found later, with his journal by his side, his final entry being on the weather with the jocular remark that, like Micawber, he was waiting for something to turn up ?

Was it King, the young soldier from India, as he left the dead leader Burke, to return to the possible relief of Wills; as he buried the latter but lacked strength to return for the interment of Burke?

Was it Howitt (1861), the brilliant bushman, explorer, geographer, geologist, anthropologist and administrator, acclaimed by all as a hero, as his relief party had come on the pitiful sight of the emaciated and almost unrecognisable King, and, under his guidance, had first buried, and, later, collected the bodies of the unfortunate Burke and Wills for honourable interment in Melbourne?

Was it Gregory (1855–6), the man who, according to Sir Hugh Nelson, "contributed more to the exact physical, geological and geographical knowledge of Australia than any other man", when he had been driven back from the search for Leichhardt by the pitiless and blinding ridges of sand which succeeded each other interminably to the south of the sources of the Victoria River?

Was it that prince among bushmen, McDouall Stuart (1861–2), he who surely earned "the palm of martyrdom in the cause (of Australian exploration) which lay so near his heart"; he who had never failed to bring his parties safely back to civilization; he who, on the occasion of the return from his glorious achievement in crossing the continent, had found himself apparently paralyzed and blinded with scurvy in its severest form, and yet so far from home that his party could not hope to reach it without his guiding genius? What must have been the anguish of spirit experienced by that great leader in his desperate attempt to cheat death until his purpose should have been accomplished? Conveyed for 600 miles in a rude litter slung across two horses trained to walk side by side, what must have been his reflections in his attempt to bring his party back to safety, his malady gone so far as to cause him to shrink from himself with nausea by reason of the decay consuming him even while he lived?

Was it Warburton, in 1873–1874, in the fearful passage of the waterless wastes along the 20th parallel as he struggled apparently hopelessly in his march against death by hunger and thirst towards the ever elusive salvation awaiting his party on the Oakover?

Was it Giles (1873–1874), leading a forlorn hope, with Gibson, into the waterless desert west of the Rawlinson Range, and forced to return alone to Tietkens and Andrews, his companion, Gibson, having perished in the wilderness?

From such an army of noble spirits, it would indeed be difficult to select one as being foremost in courage and valour. Where each individual, whether master or servant, as Sturt reported officially of his own party of 1844–1845, was little less than a hero—as for example, his servant Davenport, who, when solemnly enjoined by Sturt, supposedly *in extremis*, to deliver the copper specimen, abovementioned, to Queen Victoria, replied "Not only shall it be delivered to Her Majesty, but I will bring you yourself also to safety"—the heroes of scientific exploration in other countries would be hard put to it to surpass the courage, chivalry, and self-denial of the Australian explorers in their struggles against famine and thirst in the desert.

Such then were the actual conditions under which our earliest geographers and geologists toiled. The writer, more than twenty years ago, had been relating the stories of Eyre, Sturt, Stuart, Kennedy, Gregory, Burke and Wills, Howitt, and others, to a group of American scientists. At the conclusion of the recital, and while the company appeared somewhat puzzled, wondering whether these things had really happened, or whether the story-teller had not been carried away unduly by enthusiasm for his compatriots, it so happened that a distinguished American geologist, who had himself travelled in arid Australia, assured his fellow countrymen that there were many men in Australia who had accomplished feats equally wonderful with those of the United States explorer J. W. Powell down the Colorado, the only difference between their exploits appearing to lie in the fact that Powell had a foaming torrent, a river gone mad,

as it were, a torrent of mud and sand, as his most formidable obstacle, whereas the main enemy of the Australian explorers lay in the " absence " of water and of food.

But, even with these incredible handicaps, the geographical and geological results obtained by these heroes were far from inconsiderable, despite the relative neglect into which they appear to have fallen. It may be sufficient to give a single illustration, namely that of Sturt. The keenness of Sturt's powers of observation and reasoning will be appreciated still more when we come to mention the state of geological knowledge generally obtaining at the time.

Sturt, a pioneer of the highest rank, spent his life in the advancement of his adopted country, Australia. Sir Roderick Murchison, as President of the Royal Geographical Society, said of him in 1870, " Of the many hardy and energetic men to whom we owe our knowledge of the interior of Australia, Charles Sturt is, perhaps, the most eminent ". In the period 1828–1831 he " corrected Oxley by proving that the superfluous waters of the western slope of the Blue Mountains were drained by the River Murray, and thus achieved a most important discovery. In 1829 he followed the Murrumbidgee to the Murray, and thence to Lake Alexandrina " (Tate). The fossil Mollusca, Polyzoa and echinoids he found in the Murray cliffs he referred to species of the Eocene of England, France and Germany. Although all his specific identifications of these forms were wrong, nevertheless the species found by him were so closely allied to the European forms with which he identified them that his stratigraphical correlation was right.

In 1840, in a lecture, Sturt summarized the results of a decade of geological observations by himself in eastern Australia. " The primary rocks are the receptacles of the richer ores....Besides coal, many slates of the carboniferous formation contain also beds of iron ore.... " He sketched the general structure of south-eastern Australia as seen by himself, commencing with the central sandstone and basalt of the Sydney and Blue Mountain areas ; referred to the ring beyond these of the coal and " trap " formations of Illawarra and the north ; and still beyond these again the belts of granite and so on...." the former making glad Illawarra and the Hunter the latter fertilising the pastures of Argylle ". He described the limestones and the caverns therein of the Wellington and Molong areas, with the various marsupial bones " some larger than any now existing. No bones, however, occur of any species foreign to the continent." He described the fossil banks of the Murray, whence a slope of slight angular value carries the highly fossiliferous strata to a height exceeding three hundred feet above sea level. He pointed out how the beautiful state of preservation of the dense mass of shell and coral remains had led him to ascribe a recent age to the strata, but " on my late visit to the Murray I found embedded, a foot above the water, in rocks under cliffs a hundred feet high, a solitary shark's tooth, and near it a nautilus. Both these remains argue for that formation an older date than the apparent newness that some of the shells had led me at first to ascribe to it." From these, and numerous other observations, he concluded that Australia had once consisted of an archipelago of vast and ancient rock masses ; that the sea, separating eastern and western Australia, in the not distant geological past, had receded and had been succeeded by fresh-water lakes, inland seas and immense swamps, which effectually maintained the separation of Australia into two vast provinces, namely east and west ; furthermore, that this isolation was still maintained by desert conditions which had supervened on the marked pluvial conditions of the immediate past speaking geologically.

During his famous expedition of 1844–1845 to determine, among other things, whether traces of this ancient inland sea existed, he made extensive collections of rocks and minerals in the Broken Hill district. Especially attracted

was he by the giant outcrops of magnetite and hæmatite which he encountered a few miles north-east of Broken Hill. He does not appear to have been fortunate enough to have crossed the Broken Hill Lode outcrop itself. Had he done so, it is highly probable that he would not have failed to bring it under the notice of the mining world.

He made clear-sighted references to the striking topography of the Mundi Mundi hills, a little distance north-north-west of Broken Hill, but he ascribed the alignment of the basal points of the steep fault scarp overlooking the Mundi Mundi Plain to the action of the ocean beating on a rocky shore. This cliff feature, in the light of modern knowledge, appears to be the result of erosion on a local dislocation of the rock masses.

Sturt was much puzzled also in attempting an explanation of the extensive outcrops of what are now known to be great fluvio-glacial wastes which form a considerable proportion of the hill masses around Poolamacca, to the north of Broken Hill. He confessed his inability to explain the origin of this apparent chaotic hardened agglomeration of huge boulders, angular masses, and small ill-assorted rock fragments, all set in a finely-textured matrix of unstratified nature. His difficulty was but natural, as nothing was known at that time concerning ancient glacial climates, and indeed Agassiz and Charpentier had only just demonstrated the origin of the widely spread European " drift " which, up to that time, had been explained generally as the result of the Noachian Deluge.

Tate pays him a definite tribute—" From independent observation, I had arrived in 1879, at much the same conclusions as Sturt, though from different premises. At that time I was not aware of his labours....and now make this tardy acknowledgment of Sturt's instinctive grasp of the nature and origin of the Lake Eyre Basin....Consequently, I have elsewhere expressed the opinion that the isolation of West from East Australia, which existed while Central Australia was a marine area, was continued into late Tertiary times, not by geological, but by climatic conditions—by conversion of the depressed area into a vast fresh water sea, to be followed in our own time by utter desiccation...." (Tate, 1893, pp. 43–44).

" A tribute is due to Sturt's scientific merit and sagacity....He stands pre-eminent among land explorers for the accuracy of his observations, evincing the most patient and thoughtful investigation, for the great power of generalisation which throws a charm over all his narratives, and for his highly philosophical deductions. Sturt never received in his lifetime the honour which was his due ; and much of his geological work and speculations have either been overlooked or ignored, because it was thought (geology being then in a not very advanced state) that he was not a very experienced geologist " (Tate, 1893, p. 17).

(ii) Backwardness of Geological Science.

Having glanced briefly at the physical difficulties under which the pioneer explorer-geologists laboured, it will be helpful now to take a passing look at the state of geological knowledge at the time of the early explorations.

At the time of Governor Philip's landing (1788) in Sydney, the science of geology was decidedly backward. The word " geology " itself does not appear to have been employed till 1778. It is true that even in those early days there were original observers who had the courage to announce their ideas to the scientific world. Giovanni Arduino (1713–1795) had classified rocks in the north of Italy under the heads of Primitive, Secondary, Tertiary, and Volcanic. J. G. Lehmann, from a study of rocks in Germany, about 1752, had grouped them somewhat similarly as Arduino had done for the Italian formations. In the Harz and surrounding districts, he had found rocks crumpled with steep and vertical dips which formed the mountains. These he considered as con-

temporaneous with the formation of the earth. Upon these, with sub-horizontal or moderate dips, he had recognised a younger or secondary group containing numerous traces of animals and plants. Giraud-Soulavie (1752–1813) had told of the wealth of information contained in the limestone outcrops of the south-east of France. In the lowest beds he had found fossils, none of which, however, appeared to have any living representative. These were his Primordial rocks. In the group next above these he had noted that some of the fossils resembled modern forms, while others appeared to be extinct. This was his Secondary group. His Tertiary group contained shells which might be confused with existing species. Associated with these three groups were carbonaceous shales and slates with vegetable remains. This comprised his fourth series; his fifth series was still younger.

Important observations had been made also by G. C. Füchsell (1722–1773). From actual field work in Thuringia, he had come to the conclusion that there was a general order of succession in the stratified rocks; that they differ from each other in their fossil contents; and that they evidence the alternation of sea bottoms and land surfaces in one and the same area.

Nor among these men of vision must we forget names such as Guettard, Desmarest, Buffon, Lamarck, Hutton, and William Smith. Omitting, for the present, the names of Lamarck, Hutton, and Smith, it may be shown that Guettard (1715–1786) had demonstrated the actual origin of the basalts, of the Auvergne in France, as lavas. From 1751 onwards he had published his famous descriptions of fossils found in France, in which he had shown not only the structural relations between fossils and living marine animals, but also the great similarity of the accidents which had happened to their forms. From these observations he had inferred that the regions examined by him had been alternately land surfaces and sea bottoms. Desmarest (1725–1815) refused to take part in the absurd speculations existing concerning the origin of basalt and other lavas, but simply said " Go to the Auvergne and see for yourselves ". To him seeing was believing; the lavas could be seen to have been poured out in a molten state. Buffon (1707–1788), as Palissy (1510–1588) before him, also had made magnificent contributions to geology, especially by drawing attention to fossils as being records of the former conditions of the earth's surface; nevertheless, the necessity for keeping one eye, as it were, on the Sorbonne, while trying to tell the truths of Nature, caused his writings to lose their proper weight, and to accomplish no more towards a revolution in world thought than the mild plop of a smooth pebble dropped gently into a large water surface can set up storm waves therein.

Desmarest also appears first to have perceived how land forms have been sculptured by the action of weather, streams, glaciers, and waves, while de Saussure, Hutton and Playfair somewhat later had perceived the part these activities played.

But these, as others also, were but as mere voices raised in the wilderness; their illuminating and clearly-stated records lay musty and unheeded on the book shelves of the learned societies. There they awaited the genius of a later generation to recognise their merit. The world was still unprepared for their revolutionising ideas. The weight of tradition and religious " revelations " was opposed definitely to their acceptance. Fossils themselves were regarded variously as mere " freaks of Nature ", devoid of connection with organic life; as peculiar imitations of organisms; as creations of Satan; as shells cast by pious pilgrims *en route* to shrines; as evidences of Noah's Flood. Buffon had stated his case so guardedly for the apparently great age of the earth, and for the grand rôle played by fossils, that he raised no storm of opposition either from officialdom or from religion.

But it was not the force of popular tradition and of clerical authority alone which permitted the magnificent conceptions of these early geniuses to suffer neglect for so many years. Besides these adverse influences there was the weight of the authority of certain recognised leaders in geology. Especially was the influence of Werner (1749–1815) a block to true geological progress. He, a recognised leader, maintained the old doctrine of a primeval ocean forming an unbroken envelope to the globe. From this ocean the various rocks of the earth had been deposited in a definite order. Granites, granitoids and other plutonics had been deposited from the ocean while it was extremely hot. Werner followed Buffon in regarding volcanoes as relatively modern features which had been unable to function until vegetation had been accumulated and buried in quantities sufficient to maintain the heat necessary to support volcanism. Buffon himself estimated the age of the earth as not less than 70,000 to 75,000 years, and that the first volcanoes could not have come into being until the earth was about 50,000 years old, thereby allowing time for vegetation to be accumulated in masses sufficient to maintain the volcanic fires.

Werner classified rocks into Primitive types, such as granite, diorite, serpentine, gneiss, schist and lavas ; Transition types, these being chemical in part and mechanical in part, fossil-bearing rocks being included ; Flötz, mainly detrital in nature ; and Alluvial types, including sands, muds, clays, gravels and peats. In his opinion the granitoid, gneissic and basaltic types had been precipitated chemically from a very hot ocean. Deposition under conditions of less heat had given rise to limestone, shale, sandstone, conglomerate, slate, and so on. In his opinion the dry lands had appeared by reason of the subsidence of the ocean. Buffon came to his rescue on this point in 1778, maintaining that the ocean level had fallen by its disappearance into vast subterranean caves. Werner himself seemed inclined to think that portion had been drawn off by the approach of celestial bodies. He also met the difficult problem of folding and related phenomena by insisting that the rocks precipitated during the earliest stages had been deposited with their present attitudes, moderately inclined in places, crumpled, and even standing on end in others to form the mountains ; rocks deposited later were less steeply inclined, while these passed successively from forms possessing moderate dips to those that comprised the flat plain-alluvium.

Gradually, however, in spite of the general outlook and teaching of the leading academicians, the leaven of the findings of the great field observers mentioned above began to take effect. Space forbids more than brief mention of Hutton, W. Smith, Lamarck, Cuvier, Brongniart, von Buch, Lyell, Murchison, Sedgwick, and Logan.

Hutton (1726–1797) sought to interpret the past history of the earth in terms of present-day activities. The evidence for his belief lay in the relics of successive marine and dry land conditions observed by him in continental areas. He supplied field evidence also for his belief in the intrusive nature of granitoid and other igneous rocks. He distinguished between Primary and Secondary rocks, and he showed not only how the present land forms owe their shapes mainly to the sculpturing action of the weather, the streams and the waves, but that the waste derived from the wearing down of the hills has been distributed at lower levels to form the sedimentary rocks, and that there have been cycles of this action with sea and land conditions alternating. It was just his magnificent physiographic conceptions which were ignored by his countrymen until Jukes recognised their value in 1862. In the meantime, the American geologists, working in an area from which demonstration might be expected naturally to arise, rediscovered the principles for themselves.

Lamarck (1744–1829), the founder of invertebrate palæontology, evolved a system of organic evolution to explain the successive progress of organic forms.

In this keen perception of Lamarck's, one notes an immense advance in geological knowledge. Notwithstanding this, he, in his attempt to explain the wide distribution of marine fossils at great elevations, imagined that the ocean basins had been formed by marine scouring, and that the sea was slowly eating away the eastern margins of the lands and redistributing the waste on the western sides.

Cuvier (1769–1832), father of vertebrate palæontology, together with Alex. Brongniart (1770–1847) worked out the details of succession of the Tertiary formations of the Paris basin (1808), and showed how each is characterised by distinctive fossils.

William Smith (1769–1839), however, long before the published work of Cuvier and Brongniart, independently had discovered that the component members of the Tertiary and Mesozoic formations in England were each distinguished by a peculiar assemblage of organic remains, and that they could be arranged or distinguished in correct vertical succession merely by the knowledge of their fossil contents. Smith produced an excellent geological map of the large tract of country he had examined, and the work of this, the " Father of English Geology ", laid the foundation of stratigraphical geology, in England at least.

Of these great attacks made on the academic outlook, that of Lamarck was particularly telling. He was outspoken where Buffon, as it were, was apologetic ; he was the ardent supporter of the principle of successive and continuous advance in complexity of organic structure and awareness, whereas Cuvier invoked a succession of great world catastrophes to account for the breaks in the geological record. The Uniformitarians, however, who carried the splendid conception of Hutton and Lamarck to extremes, failed to recognise any marked variation from present earth activities on the part of past agencies ; moreover, they failed to see why fossils of the higher types of life such as those living today should not be found in the most ancient rocks. Lyell (1797–1875) was the leader of this school, one far behind that of his great predecessor Lamarck. The clearing up of this tangle, in 1859, by Darwin was far later than the times with which we are here dealing.

Some of the greatest hammer blows dealt against the image revered by the conservative geologists of the Neptunian School were those by Leopold von Buch (1774–1853), the most promising pupil of Werner himself, and the " most accomplished geologist in Europe ". Full of zeal for the teachings of his master, Werner, he travelled to various European areas to prove their validity. In Italy and the Auvergne areas, however, he was converted to the views of Desmarest and Guettard. In Norway he found granitoids actually intruding the sediments. Years afterwards, he—whom Humboldt described as the greatest geologist of his day—visited the British Isles, travelling on foot, to examine the various geological sections for which Britain was famed. His whole wardrobe on this trip is said to have consisted of an ordinary suit, surmounted by an overcoat (whose large pockets were filled with papers and geological instruments), one shirt, a handkerchief, one pair of socks, one pair of boots. When necessity demanded, and opportunity offered, for a clean-up he would wash the shirt and socks and wait round for them to dry.

As a result of the observations made by von Buch on these travels, the doctrine of the Plutonists came rapidly to the front. Finally the influence of the observations recorded by Smith, Hutton and others led to such grave distrust, in England, of the irresponsible speculations of the traditional school, that in 1807 the Geological Society of London was founded, its avowed intention being to make records of observations actually and carefully conducted in the field.

With the emphasis thus placed upon field work, geological science made rapid and great advancement. Murchison (1792–1871) mapped the folded

geological complex of south Wales, and introduced the term Silurian about 1835 as a distinctive mark for a definite large division of geological time. Sedgwick (1785–1873) contemporaneously applied the term Cambrian to a still more complicated rock group in north Wales underlying Murchison's Silurian. It was not till a generation later (1879) that Lapworth proposed the term Ordovician to include the upper beds of Sedgwick's Cambrian, together with the lower beds of Murchison's Silurian. Again, it was as late as 1839 that Murchison and Sedgwick gave the name Devonian to a distinctive group of rocks immediately overlying the Silurian, and it was as late as 1841 that Murchison gave the name Permian to the world. Logan (1798–1875) at a period somewhat later than 1842 discovered rock formations unconformably underlying the Cambrian. Darwin's *Origin of Species* was published much later even than the discovery of gold and the founding of the first grand geological survey, in Australia.

At a time, then, when the origin, structure and even the position in time, of the great geological complexes of regions such as Cornwall, Devon, Wales, the Lake District of England, Scotland, France, Germany, Italy and other countries were still unknown, the early explorers of Australia were conducting their geographical and geological observations.

These notes serve not as apologies for the apparent scrappiness of the geological notes by the explorers, but as indications rather of the geographical and geological insight possessed by many of them, even though they had not the opportunity—in far-off Australia—of becoming acquainted readily with the advances that were being made in mining, stratigraphical, and structural geology in the northern hemisphere. They had to rely mainly upon the geological information which they had acquired before arriving in Australia, together with their own undoubted powers of observation.

Part II. State Geological Surveys and the Australian Universities.

It was the discovery of gold and other valuable materials in commercial quantities which led, in very great measure, to the founding of the State Geological Surveys and the Australian Universities. Gold had been discovered in New South Wales by McBrien in 1823, by Strzelecki in 1839, by W. B. Clarke in 1841—who also had announced the presence of tin in 1849—and, in payable quantities, in 1851, by E. H. Hargreaves (1816–1891). Thereafter the search for it and for other valuable minerals had proceeded with incredible speed. Prospectors had flocked into this great unknown land of Australia from all points of the compass. Every class of country indifferently had been examined by them. It mattered not whether it was the harsh broken face of the Australian Alps, swept by frequent raging storms ; whether the profound gorges dissecting the far-stretching tablelands of the eastern States ; the interlacing jungles of the coastal tropics and of the west coast of Tasmania with their desolating insect pests ; the fever-stricken rivers and swamps of the far north ; the irregular slopes leading to the interior of the continent ; the drought-stricken interior itself, with its heat, desiccation and barrenness ; all these strange and forbidding regions alike had been attacked by the hardy pioneers in their feverish hunger for gold. Enormous wealth, even in 1851, had been extracted from many places in Victoria, both from alluvial and " reef " gold, and it became increasingly apparent to the governments of the day that the growing complexities of the legal, economic, social and scientific situations which had arisen should be faced courageously and settled satisfactorily. Much more apparently was needed than the part already played by Strzelecki, Clarke and Hargreaves. Strzelecki himself, in 1845, had advocated strongly the founding of a geological survey by the govern-

ment. W. B. Clarke also had persistently advocated the formation of an official geological survey.

Following on their urgent representations came the appointment of official surveys in New South Wales and Victoria, while, considerably later, the State surveys of Queensland, South Australia, Tasmania and Western Australia came into being.

The need for instruction in geological principles was met, in part, by the founding of the State Universities. Lectures commenced at Sydney University in 1852, Melbourne 1855, Adelaide 1876, Tasmania 1892, Queensland 1911 and Western Australia 1913.

It may now be of interest briefly to trace the procedure observed in the establishment and conduct of these institutions. We may commence with the New South Wales survey.

New South Wales. Count Strzelecki's recommendation to form an official survey was associated with Clarke's unceasing advocacy. This led to representations being made to the British Government. Sir Charles Augustus Fitzroy, the State Governor, in March, 1849, petitioned the Right Honourable Earl Grey : " I am desirous of bringing under your Lordship's notice the expediency of causing a Mineral and Geological Survey to be made of the colony in order to determine the mineral resources which it may possess. The subject has extensively engaged the public attention for several years past in consequence of the great success which has attended the opening of some of the copper mines in the adjoining colony of South Australia....in order to show the probability that if the country were examined by a competent geologist....valuable metalliferous ores would be discovered, which would not fail to add greatly to the resources of the colony, extensively to benefit the land fund, and thus to open out a new field for British immigration...."

The urgency was recognised by the Home Government, and Sir Henry de la Beche, Director of the British Survey, was asked to nominate a suitable person. The salary suggested was £600–£700 a year.

J. Beete Jukes was recommended by reason of his knowledge of Australian geology ; he declined the offer. William Bristow was then recommended at a salary of £600 a year ; he accepted, but resigned later because of " certain family matters ".

Lord Grey thereupon corresponded again with de la Beche : " Lord Grey would be glad if you should be enabled to secure the services of some properly qualified person, but as so long a time has elapsed since the Governor of the Colony expressed his anxiety on the subject, I am to add that it will be indispensable that anyone selected for the duty should engage to start without delay ".

Samuel Stutchbury was recommended, and the conditions of appointment left Mr. Stutchbury free to determine the work to be done and the order in which the survey should be conducted, with the exception that the known mineral-bearing areas were to be examined first, and these were indicated for his guidance. Quarterly reports and accompanying maps were to be furnished indicating the structure of the areas examined. Specimens were to be provided for the Australian Museum, a portion of the Northern Wing of which had been completed in 1849. The equipment was " to consist of two men, a spring cart, two horses, harness, two saddles, and two bridles ". Stutchbury arrived in New South Wales in 1850, and spent two years, approximately, in company with Hargreaves, investigating the gold discoveries. Later on he reported on the Ipswich Coal Measures, Queensland being then in the colony of New South Wales.

Stutchbury resigned in 1855. Jack and Etheridge stated that his work is not so well known as it should be, and that he was one of the " three worthy pioneers in Australian geology ". Mr. W. Keene, Examiner of Coal Fields,

" continued, in a certain sense, the geological survey, but the actual advancement in our knowledge of stratigraphical geology and palæontology is due to the Rev. W. B. Clarke, and to him alone " (Tate).

In 1873 C. S. Wilkinson became Geological Surveyor, and in 1875 the Mines Department was reorganised with Wilkinson as head of the new Geological Survey Branch, a position which he held till his death in 1891. In 1891 E. F. Pittman became Government Geologist. A prominent senior member of that survey was J. E. Carne, who joined the survey in 1879 and became Government Geologist in later years. To Carne is due the credit of initiating the idea of the excellent " Mineral Resources " Series. T. W. E. David joined the survey as Geological Surveyor in 1882.

In 1880 the Department of Mines issued the first geological map of New South Wales (based on the original map of the late W. B. Clarke).

Victoria. The geology of Victoria was little more than a blank till 1853. Mitchell, Strzelecki and Jukes had made valuable notes, but these were either misunderstood or ignored. Then came the discoveries of gold in the State in 1851, causing considerable embarrassment to Lieutenant Governor Latrobe, because of lack of competent advice " respecting gold in Victoria ".

As a result of Latrobe's representations a Geological Survey was appointed in 1852 under the direction of A. R. C. Selwyn, " one of the ablest of the staff of the Geological Survey of Great Britain ". Associated with him were C. D'Oyley H. Aplin, Richard Daintree, C. S. Wilkinson, G. H. F. Ulrich, Norman Taylor, H. Y. L. Brown, R. A. F. Murray, R. Etheridge and E. J. Dunn, all field geologists. F. McCoy, Professor of Natural History in the University of Melbourne, was appointed palæontologist, while Cosmo Newberry was chief analyst. The work accomplished by this survey, until its close in 1869, was, perhaps, unsurpassed in quality by any survey in existence. Through its efforts insight was gained rapidly into the geological structure of Victoria generally, and an area, exceeding 3,500 square miles, was surveyed geologically in detail and illustrated by means of 65 excellent maps, each including an area of 54 square miles. These maps were reproduced on a scale of two inches to a mile. In 1863 a general sketch map was published at eight miles to an inch. This was reproduced in 1867 to a reduced scale. The Silurian, Upper and Lower Ordovician (known then as Lower Silurian, the term Ordovician not being employed till 1879) were recognised, and their mutual boundaries surveyed ; the Middle Devonian, Upper Devonian and " Carboniferous " were recognised and surveyed ; while the coal measures of the Cape Otway and Western Port districts were classified as Jurassic. These determinations have stood the test of time, but the work on the Permian and the Tertiary has been modified definitely ; these determinations, however, were not due to errors on the part of the field officers, but to mistaken identifications by the palæontologists.

This geological survey, " one of the most complete ever organised " according to Tate, was disbanded in 1869. Selwyn became Director of the Geological Survey of Canada, while other members of his excellent staff went to various States—Daintree and Aplin to Queensland, Wilkinson, Etheridge and Pittman to New South Wales, Ulrich to New Zealand, Dunn to South Africa, Brown to Western and South Australia.

In 1871 the need for a continuance of the survey was felt keenly, and it was resumed under Brough Smyth, who was succeeded by J. Couchman, the Secretary for Mines, as Smyth had been before him. Field work was continued by F. Krausé, R. A. F. Murray and Norman Taylor, with A. W. Howitt as Gold Fields Warden, and W. Nicholas. During this period geological maps, together with the reports, of the principal gold fields, were published, while a sketch map of Australia was issued departmentally by Smyth.

In the beginning of 1878 the survey was discontinued again, but was resumed later, Murray alone being appointed. In 1887 James Stirling was appointed in charge of the survey. No organised surveying had been carried out since 1877. In 1889, however, A. W. Howitt became Secretary of Mines. He had become well and honourably known by his outstanding geological work in eastern Victoria.

Queensland. The State of Queensland remained as a part of New South Wales until 1859, and the earlier official geological work was conducted by Stutchbury and Clarke. In 1868 C. D'Oyley H. Aplin was appointed Geologist to southern Queensland, and Daintree Geologist to northern Queensland; Daintree and Aplin had been senior members of Selwyn's staff in Victoria. Aplin relinquished his position in 1870, while Daintree, in 1871, went to London in charge of the Queensland mineral exhibits at the 1872 exhibition. Daintree accomplished much for Queensland geology. He outlined the geology of the State in the Quarterly Journal of the Geological Society of London for 1872, illustrating his report with a sketch map. He relegated much of the Silurian of previous observers to the Middle Devonian; he recognised the Coal Measures of northern Queensland as "Carboniferous" (Permian); the coal containing *Tæniopteris* was referred to the Mesozoic; the Ipswich coal was grouped with the Jurassic, and so on. His work is considered as substantially correct today, subject to the raising of some of his Devonian into the Carboniferous and to the relegation of the Desert Sandstone to the Upper Cretaceous.

A. C. Gregory, who had been Surveyor-General for Queensland, was appointed Geologist for southern Queensland in 1875. He carried out valuable work on the southern coal fields.

R. L. Jack, who had served for ten years on the Scottish Geological Survey, was appointed Geologist for northern Queensland. Upon the retirement of Gregory in 1879, he became head of the survey for the whole of Queensland. Rands joined the staff in 1883, and Maitland in 1888.

The publication of the "Geology and Palæontology of Queensland" in 1892 by Jack and Etheridge was a valuable contribution to the geological knowledge of Australia. As Tate says, "It stands unrivalled for its rich stores of information and for its methodical arrangement, tracing as it does the various steps in the growth of our knowledge, and giving credit to each previous observer who had contributed to its history".

Western Australia. Active mining operations in Australia, as mentioned above, date from 1842, when lead and copper mines were first discovered and worked at Wanerenooka, in the coastal strip about three hundred miles northerly from Perth. Dr. Ferdinand von Sommer was employed as the official geologist during the period 1847–1849. He examined the Victoria, Toodyay, York and Mt. Barren districts.

After the expiry of von Sommer's term of office, there ensued an interval of twenty-one years, during which excellent geological observations were made by the explorers A. C. and F. T. Gregory.

H. Y. Lyell Brown was Government Geologist from 1870 to 1872. In addition to the preparation of three geological maps and ten reports, Brown's advice led to the discovery of artesian water a few miles south-east of Perth.

Nine years after Brown's retirement, E. T. Hardman, of the Geological Survey of Ireland, became Government Geologist. He was the pioneer geological observer for the far north of Western Australia, and his work in the State was confined mainly to the "Kimberley District, upon which he issued two voluminous reports illustrated with a series of geological maps". His field work, carried out during 1882–1884, "laid the foundation of our knowledge of the geology of the Kimberley district". Hardman returned to the Irish Survey in 1885.

In 1887 H. P. Woodward, who had served upwards of three years with H. Y. L. Brown, was appointed Government Geologist, a position which he held until 1895. In 1894 he published a geological map of the State.

In 1896 the Survey, as at present constituted, was created, with A. G. Maitland in charge, who had received an excellent training, from 1888 onwards, in Queensland, under R. L. Jack. Maitland's work in Western Australia, conducted under conditions of extreme hardship and danger, entitles him to a place among the great pioneers.

South Australia. This State for many years remained without an organised geological survey. Sturt had acted in an honorary capacity, and urged the need of scientific prospecting for valuable minerals; indeed, during the whole of his great exploring trip of 1844–1846 to find the centre of the continent he sought assiduously to discover minerals of commercial value. In 1844 the copper of Burra Burra had been found, while Sturt himself was in the Broken Hill district, having just missed the great "Lode" only by a few miles, his actual route crossing what is now Piesse's Knob and the Stephen's Creek Reservoir a little to the north-east.

Selwyn, in 1859–1860, while examining the greater Adelaide area, had discovered a glaciated pavement without, however, determining its age. The rock formations of the large district examined inclined him to believe that they might "be grouped under three distinct and unconformable formations".

In 1864 E. H. Hargreaves conducted extensive trips in the State in search of workable gold deposits. Somewhat later (1872) Ulrich reported on the mineral resources of the country lying to the north of Port Augusta. In 1882 Tate described the geology and botany of the Northern Territory, which was then part of South Australia, and in the same year H. Y. L. Brown became Government Geologist of the State, retiring in 1912. Skeats says of this pioneer, "His were the first geological observations placed on record with regard to many of the remote regions of the interior. Many of his journeys were undertaken with only an Afghan camel driver for a companion and under conditions of severe hardship. His written reports were very brief, but his great contribution lay in the preparation of maps, notably the geological map of South Australia, published in 1899. No geologist has commanded, to a greater degree than H. Y. L. Brown, the confidence and respect of all sections of the community—from the governments that were guided by his recommendations to the individual prospectors who looked to him for advice, and who still treasure the memory of his words of encouragement."

Tasmania. The official Geological Survey of Tasmania is a product almost entirely of the present century. W. H. Twelvetrees was appointed Government Geologist and Chief Inspector of Mines in 1899, and Director of the Geological Survey from 1914 to 1918.

Geological work, previous to Twelvetrees' appointment, appears to have been conducted mainly by R. M. Johnston (1845–1918). Johnston was not the official geologist of Tasmania, being employed officially as Government Statistician and Registrar-General from 1881–1918, but, as opportunity offered, he laboured hard as a field geologist, and produced a magnificent volume, "The Geology of Tasmania", of 408 quarto pages, in 1888.

G. A. Waller was Assistant Government Geologist in 1901, and continued as such till 1904. Waller contributed much to the knowledge gained concerning the stratigraphy of the Lower Palæozoic rocks of the West Coast area, and he applied modern methods in approaching the complex mining problems of Tasmania. He was succeeded by L. K. Ward (1907–1911) and by L. L. Waterhouse (1912–1916). The names of these later workers are included here because of the excellent results obtained by them, working under very great disabilities,

occasioned not only by the complexity of the geological problems involved, but in great measure also by the excessively rugged and mountainous nature of the topography, together with the exceptionally severe and harsh climatic conditions experienced.

The Universities. Mention is made here only of the Universities of Sydney, Melbourne and Adelaide; the Universities of the remaining States not being considered as having been founded within the Heroic Period of Australian geological work.

The University of Sydney was opened for classes in 1852, but the subject of geology was not included in the curriculum until 1866, when A. M. Thomson was appointed Reader in Geology and Mineralogy and Professor in 1870. He was succeeded in 1872 by A. Liversidge, whose main interests, however, lay in the realms of chemistry and mineralogy. W. J. Stephens, in 1882, became Professor of Natural History and Lecturer in Physical Geography and Geology. In 1891 T. W. E. David, who previously had been the Senior Geological Surveyor on the staff of the Geological Survey of New South Wales, was appointed to the Chair of Geology.

The real advance effected in geology up to 1872 was not due to university effort, but to W. B. Clarke, working officially with the Government but unofficially with the University and with scientific societies. From 1872 onwards splendid progress was made under Liversidge, Clarke, Wilkinson and David. Science in Australia owes more to the herculean efforts of these workers than is generally known. In season and out of season, Clarke urged the value of field geology, of education in geological principles, and the value of scientific societies. Liversidge, in addition to his lectures and research work, was an ardent supporter, with Clarke, of scientific institutions such as the Royal Society. He was the prime mover and guiding spirit both in founding and carrying on the Australian and New Zealand Association for the Advancement of Science, becoming president in 1898 of that Association. Wilkinson maintained the grand traditions of the Victorian survey under Selwyn. David, besides being an enthusiastic field geologist, was, in common with Clarke, Liversidge and Wilkinson, a true friend of science generally. Science in Australia found in him one of its greatest champions. Geology was his special choice, but during all his official life he strove for the attainment of three objectives, namely to understand the geological history of Australia, to inculcate a love for science generally in the public mind, to remove the disabilities under which science generally, and scientists individually, laboured in Australia. He was president of the A.N.Z.A.A.S. in 1904 and 1914.

The University of Melbourne began lectures in 1855. F. McCoy, the Professor of Natural Science, was one of the four foundation professors; he was a trained palæontologist before arriving at Melbourne University. In 1844 he had published his "Synopsis of the Carboniferous Limestone Fossils of Ireland" and in 1846 he had issued a "Synopsis of the Silurian Fossils of Ireland". On arriving at Melbourne, he found that he was expected to attend to the interests of comparative anatomy, botany, chemistry, geology, mineralogy and palæontology. For a period exceeding forty years he did lecture on, at least, botany, geology, palæontology and zoology. He was awarded the Murchison Medal of the Geological Society of London in 1879. As Palæontologist to the Geological Survey of Victoria he was of great assistance to Selwyn's Geological Survey of Victoria. McCoy also advanced the cause of science in Victoria by founding and directing the Museum of Natural History and Geology in Melbourne. Additional references to his work are made later under the head of The Permian Problem.

The University of Adelaide commenced lectures in 1876, with R. Tate as the Elder Professor of Natural Science. Tate previously had distinguished himself as a botanist, geologist and palæontologist, and had been awarded the Murchison Medal of the Geological Society of London as far back as 1874. He became one of Australia's foremost geologists and botanists. His name is inseparably connected with many of the excellent publications on the Tertiary and Recent marine fauna of South Australia and Victoria. He was the first to discover Cambrian rocks in South Australia (1879) besides proving definitely the occurrence, in that State, of great areas of Pre-Cambrian rocks. He worked enthusiastically for science generally, taking a leading part in founding the Adelaide Philosophical Society and the Royal Society of South Australia. He was President of the Australasian Association for the Advancement of Science in 1893. His presidential address on the occasion of his inauguration was a summary—a magnificent contribution—of geological progress in Australia from 1788 to 1893.

Part III. Some Geological Pioneers hitherto Inadequately Recognised.

In the "David Lecture" of 1933, to the Royal Society of New South Wales, E. W. Skeats satisfied, in great measure, a long-felt want by assembling summary statements concerning the work and personalities of "Some Founders of Australian Geology". To this publication the reader is referred for information concerning the majority of the pioneer geologists of Australia. There are a few others, however, whose names do not figure in the list given by Skeats, but whose work appears to entitle them to individual recognition. A few notes also additional to those furnished by Skeats are supplied on individual workers in other portions of this lecture. These remarks, dealing with recognised pioneers, apply particularly to C. Sturt, W. B. Clarke, F. McCoy, A. C. Gregory, R. Tate and T. W. E. David and are purely supplementary to those of Skeats. The list following contains the name of no person living with the exception of A. G. Maitland and, in one instance alone, is mention made therein of any worker whose Australian work commenced as late as 1900. The exceptional instance is that of J. W. Gregory, who had had a long and distinguished career as geologist and writer before following McCoy as Professor of Geology at Melbourne University. The names of these workers are Péron, Stokes, Howchin, Dunn, Carne, Maitland and J. W. Gregory.

Francois Péron. The French expedition to Australia, under Nicolas Baudin (1800–1804), was contemporaneous with the great marine survey of Australia under the leadership of Matthew Flinders. Péron was the senior zoologist and the author of the narrative of Baudin's expedition. He added much to the previous knowledge of the geography and geology of the continent. He pointed out the similar appearance of the southern, western and north-western coastal districts. He noted the various schists of ancient appearance on Kangaroo Island and on the King Islands, together with the covering of the Kangaroo Island primitives by fossil-bearing limestone. He perceived the significance of the raised marine Tertiaries along the southern coastal areas of the continent, and he mentioned the basal nature of the granitoids and altered sediments occurring in certain portions of the southern coast. "Few geologists have been more in advance of their age, or have suffered so long an undeserved oblivion as Péron."

Ad. John Lort Stokes. The third voyage of *The Beagle* occupied the period 1837–1843. The narrative of the long voyage was written by Stokes, who had been in charge of the expedition following on the illness of Captain Wickham. A considerable amount of geological insight is exhibited, especially in that

portion of his report concerning the capping of the primitive rocks of south-western Australia by young rock formations only ; the granitic nature of the Darling Range ; the horizontally-bedded sandstone formations overlying the slaty rock of the Arnhem Land plateau ; the cover of finely-textured sandstones to the old rocks in the Port Darwin area, and so on.

Walter Howchin was born at Norwich, England, in 1845, but did not arrive in South Australia until 1881. As a youth he was attracted to the study of geology, and he resigned his position as a clergyman in 1880, devoting his energies thenceforward to the study of geology. He was appointed Lecturer in Mineralogy at the South Australian School of Mines in 1899, and Lecturer in Geology and Palæontology in the University of Adelaide in 1902, holding that position till 1918, when he received the status of Professor of Geology. In 1920 he retired with the title of Professor Emeritus.

Howchin made notable observations on the Cambrian formations of South Australia, and on the history of glacial epochs in South Australia during Permian and late Pre-Cambrian time. His work was recognised outside his own State ; among other recognitions he received the Clarke Memorial Medal of the Royal Society of New South Wales in 1907, the Mueller Medal of the Australian Association for the Advancement of Science in 1913, and the Lyell Medal of the Geological Society of London in 1934.

Edward John Dunn was born at Bristol, England, in 1844. He joined the Geological Survey of Victoria in 1864, and received field training under the able leadership of G. H. F. Ulrich until the disbanding of the survey in 1869. He then became Government Geologist of Cape Colony, holding that position during the period 1871–1886. While in that position he carried out the first detailed geological survey in Cape Colony. In 1904 he was appointed Director of the Geological Survey of Victoria, a position which he held until 1912.

Dunn wrote extensively on the significance of past glaciations, on the significance of pebbles, and so on. To him we are deeply indebted for the admirable portrayals we possess of the personalities and work of the men who formed Selwyn's survey, that survey which Dunn quotes as being " one of the most complete geological surveys ever organised, except, perhaps, that of the United States Territories, under Dr. F. V. Haydon " (*Q.J.G.S.*, Vol. 35, Pres. Add. 52). In recognition of Dunn's contributions to geological knowledge he was awarded the Murchison Medal of the Geological Society of London in 1905.

Joseph Edmund Carne (1855–1922) was born at Melbourne. He was the second son of Joseph William Carne, of Appin and Riverina, and the grandson of Capt. T. C. Carne of Truro, Cornwall, England, who landed in Australia in 1814 as a lieutenant in the 46th Regiment. Capt. Carne married Mary Broughton, daughter of Commissary Broughton of the first fleet, who was born in Sydney in 1793.

The Carne family name is well known in Cornwall, particularly in the area between St. Columb Minor, near Newquay, and Truro. It is of interest that the most outstanding authority and writer on Cornish geology and mining, during the first half of the nineteenth century, was Joseph Carne of Penzance.

Carne's early ways were spent in the Riverina, western New South Wales, and Queensland. The family interests were mainly pastoral. In 1879, whilst droving cattle from Deniliquin to the Diamentina and Cooper Rivers, he contracted " sandy blight " in so severe a form as to threaten him with loss of sight. Almost blind, he set out for Sydney for treatment, riding 270 miles on horseback to pick up the coach, from Hungerford to Bourke, thence to Sydney by rail. Although he recovered his sight, it was permanently affected. He had become interested in geology, and while undergoing treatment for his eye trouble, he was appointed personal assistant, in 1879, to C. S. Wilkinson, the State

Government Geologist. He prepared a geological and mining exhibit for the Sydney International Exhibition in 1879, and for the Melbourne Centennial Exhibition in 1881. This exhibit was displayed in the Palace Exhibition building in the Sydney Botanic Gardens until the fire of 1882. The salvaged portion of the exhibit formed the nucleus of the Mining and Geological Museum which was then started in the Outer Domain with Carne as Curator. During his period in this office he personally took charge of mining and geological exhibits at the New Zealand and South Seas Exhibition of 1889 and the International Exhibition of London in 1890.

In 1892 he was appointed Geological Surveyor in the Department of Mines, New South Wales, and took charge of exhibits in the World's Columbian Exposition at Chicago. Much of this exhibit is still at Chicago. In 1902 he became Assistant Government Geologist, and in 1916 Government Geologist, of New South Wales, until he reached retiring age in 1919.

Early in 1912 he examined Papua for the Commonwealth Government, and reported on the prospects of various coal and mineral oil occurrences in the Fly, Kikori and Carne River districts. He included inspections of oil-bearing country in Java, Borneo and other islands during this investigation. In this work he contracted a severe form of malaria, from the effects of which he never fully recovered.

In 1920 he was awarded the Clarke Memorial Medal of the Royal Society of New South Wales. He was primarily responsible for the publications, by the Geological Survey of New South Wales, known as "Mineral Resources", to which he himself made a number of notable and widely-sought contributions, including those known as the Copper, Tin, Kerosene-Shale, and Western Coal-Field Memoirs.

Carne was one of the most conscientious, honourable and industrious of the pioneers. He was twice married, his first wife being Louisa McArthur of Norwood, Goulburn, whom he married in 1882, his second Clara Hudson, of Croydon, New South Wales, in 1895, who survives him. He had five sons and two daughters, all of whom are living.

Andrew Gibb Maitland was born on November 30th, 1864, at Huddersfield, England. His father was George Maitland, of Aberdeen, Scotland.

Maitland arrived in Australia in 1888 to take up the position of Assistant Government Geologist in the Geological Survey of Queensland under R. L. Jack. This position he held during the period 1888–1896. In 1891 his services were loaned to the British Government to accompany Sir William MacGregor in his explorations of New Guinea. He made valuable reports on the raised coral reefs and other geological features of New Guinea. He was appointed Government Geologist of Western Australia in 1896, a position which he held till 1926.

Maitland's work, in great measure, partook of the nature of exploration. He examined the various Western Australian gold fields in their pioneer stages, experiencing their hardships and dangers; in 1901 he accompanied Brockman's expedition, commencing at Wyndham and traversing the wild Kimberley Division.

Maitland was awarded the Clarke Memorial Medal of the Royal Society of New South Wales in 1927, the Mueller Memorial Medal of the Australasian Association for the Advancement of Science in 1924, the Kelvin Memorial Medal of the Royal Society of Western Australia in 1937, and he also received the great honour of honorary membership of the Royal Society of New South Wales.

John Walter Gregory was born in London in 1864. Before coming to Australia he had been an explorer, geologist and journalist of note. In 1900 he succeeded McCoy as Professor of Geology at Melbourne University. This position he held until 1904, vacating it to become Professor of Geology at the Glasgow University.

Gregory was awarded the coveted Bigsby Medal of the Geological Society of London, bestowed only upon men under 45 years of age. He was the author of *The Great Rift Valley* (Africa) and *The Dead Heart of Australia.*

The uplifting influence which he exerted upon his students, both in Melbourne and in Glasgow, was very marked. It was considered a privilege by his students to accompany him on his very long excursions. The students, for example, who visited and examined the Lake Eyre Basin with him in the height of one bad summer speak with admiration of his gifts of leadership. The writer remembers also, with keen appreciation, a trip to the central highlands of Scotland with him and his senior students in the midwinter of 1909 during a record snowstorm. He appeared to possess a magnetic influence on students generally. One of his Australian students informed the writer " Gregory did not appear to think about discipline, his lectures were so interesting that the students' attention was fixed the whole time, afraid lest some of the lecture might be missed ".

Some of his geological conclusions concerning the geology of Australia, particularly the nature of the water content of the Great Artesian Basin, together with the metamorphosed Ordovician complex of Victoria, have been subjected to correction by later field work, but his many suggestive inferences usually provoked keen discussion and led to interest being taken in the study of various problems. He accomplished excellent physiographical work in Victoria. Thus he perceived that the plateaux of the State represent a peneplain raised differentially and profoundly dissected by stream action in relatively recent geological time. He was not only an enthusiastic geographer, but also an explorer seeking to fathom the secrets of Lake Eyre, of Central Africa, of the eastern Himalaya, and of the Andes at the head of the Amazon. He was drowned in an attempt to pass the dreaded Pongo de Mainique, in the profound cañon of the Urubamba, one of the headwaters of the Amazon.

Part IV. Some Major Problems in Australian Geology.

1. The Permian Problem.
2. Glaciation in Australia.
3. Physiographic Problems.
4. The Building of Australia.

1. The Permian Problem.

The study of the Permian, with its complicated stratigraphical, biological, glacial and structural aspects, has proved one of the most fascinating of the geological problems which Australia has to offer.

In the early days of Australian geology the Permian, as a definite geological period, was not known to exist, and the controversy dealing with the points concerned in its history centred mainly round the question as to which beds should be referred to the Carboniferous and which to the Mesozoic ; later discussions (from 1849 onwards) sought to ascertain which portions of the coal measures of Newcastle and Illawarra, and their associates, were Permian and which Carboniferous, the Mesozoic possibilities being excluded. A later phase centred round the relation exhibited by certain highly folded rocks to others having a sub-horizontal attitude, and yet each apparently possessing fossil contents of Permian age.

Interest was directed first to these rocks by reason of their economic importance, seeing that the coal measures of the Sydney-Newcastle-Illawarra-Blue Mountains area were included in the formations. Bass, in 1797, had described these coal measures as having probably the structure of a large basin. The question of their age does not appear to have aroused much interest at

the time. The Permian, it will be remembered, was not recognised as a definite geological period until 1841. Even the Cambrian, the Silurian and the Devonian were not recognised as former definitive world-ranging activities until the period 1835-1839, and it was probable that Bass considered the coal of the Greater Sydney Area to be coeval with the Carboniferous of England.

The first serious attempt, apparently to determine the age of the formations containing these coal measures, was in 1821, when Dean Buckland, from specimens forwarded to him, appears to have considered the coal measures of the Illawarra-Newcastle area to be practically contemporaneous with the Palæozoic coal measures of England, that is, Carboniferous. Archdeacon Scott, in 1824, agreed with Buckland's determination of age for the Newcastle Coal Measures.

It will be remembered that Strzelecki in 1845 had attempted a classification of the rock systems of New South Wales, those of his first epoch comprising the plutonics and the altered sediments of the mountain axes; the second epoch comprising sandstones, shales, slates and limestone resting on the earlier axial formations and containing the first records of life, presumably Carboniferous, with still older forms; his third epoch being that in which the Newcastle Coal Measures had been deposited; the fourth, during which the Blue Mountains sandstones, the river gravels, the raised beaches, and so on, were deposited. Strzelecki considered the coal measures under consideration to be younger than the beds immediately underlying them and containing marine fossils.

Morris's examinations (1845) led him to relegate the plants obtained from the Newcastle Coal Measures to the Jurassic, and the associated marine beds possibly to the Carboniferous.

Long before this, however (1828), plant remains from the Newcastle Coal Measures had been examined by Alexandre Brongniart. Among them he had found some very peculiar forms to which he had given the names *Glossopteris* (*Browniana*), *Gangamopteris* and *Phyllotheca* (*australis*). With these new forms were others named *Vertebraria*. *Glossopteris* was considered to be a type of fern possessing a midrib with lateral venation therefrom, repeatedly anastomosing. *Vertebraria* was referred later to the rhizomes of *Glossopteris*. *Gangamopteris* was allied to *Glossopteris*, and at first was believed to possess no marked midrib. Now this *Glossopteris* group had not been found in the Culm (Carboniferous) flora, and to workers such as McCoy it suggested definite affinities with Mesozoic types.

McCoy now entered the discussion. Long before his arrival in Australia, this distinguished palæontologist had become interested in the problem of the age of the Newcastle and Illawarra Coal Measures, for, in 1848 (*Brit. Ass. Adv. Sci.*, 1847), he had described " seventeen fossil plants and eighty-three Mollusca " (Tate) from these formations. The plant remains were referred by him to the Oolitic group, with the note that there was no trace " of any characteristic fossil of the old coal of Europe or America ". The associated fossil shells he referred to the Carboniferous.

The next serious approach to the problem was by another outsider, namely Dana, who in 1849 suggested a Permian age for the Newcastle and Illawarra coals. He, however, grouped both the coal and the marine rocks underlying the coal, together with the sandstones and shales lying above the coal in the Sydney and Blue Mountain areas, as one great Carboniferous formation. This confusion, or rather inclusion, of the Triassic sandstones with the underlying coal measures was only natural by reason of the apparent conformity of the two great groups, and by the failure, for many years, to find fossil traces in the conformable Mesozoic group.

Jükes and Stutchbury contributed to the discussion in 1850. Jükes maintained that the coal measures and the marines were of the same age, namely Carboniferous. Stutchbury found Lepidodendron in beds underlying these.

The discussion thus occasioned concerning the age of the coal measures of Newcastle and Illawarra was carried on for years, and the matter is of such historic interest that a quotation from the Presidential Address to the Royal Society of Victoria in 1861—and apparently not at all well known today—by Sir Henry Barkly (1861) is justified by reason of the simplicity and breadth of its presentation :

" The coal measures of New South Wales, of Tasmania, and, no doubt, of Victoria also, rest upon a stratum of sandstone rock, containing marine shells and corals, of descriptions similar to those found in the mountain limestone on which the ancient carboniferous formations of Great Britain repose ; but, on the other hand, the beds of shale, in which the seams of workable coal are interspersed, exhibit fossil plants widely differing from those of the British coal measures, although it happens, strangely enough, that the remains of the true carboniferous flora are still found in various parts of Australia, but not yet, I believe, in conjunction with coal.

" Notwithstanding this discrepancy, the Rev. W. B. Clarke has always held that the plant beds of the Hunter River coalfield, are of nearly the same age as the underlying beds with animal fossils, and that neither are of more recent origin than the close of the first great epoch of ancient life on our earth, termed by geologists the Palæozoic period.

" Professor McCoy, on the contrary, published his opinion, long before coming to this colony, that a vast geological interval elapsed between the deposition of the marine remains and the ferns and cycadeous plants above them, and argued that the latter so closely resembled the species found in the Oolitic or secondary coal of Yorkshire that they must (together with nearly identical forms from the coalfields of India) be referred to the same group, or second division, of the Mesozoic or middle age of life.

" This opinion has been adopted by most of the leading geologists of the day, but that of Mr. Clarke has, nevertheless, been supported by some distinguished authorities, including Mr. Jukes, now local director of the Geological Survey of Ireland, Professor Dana of the United States Exploring Expedition, Dr. Hochstetter of the Austrian Exploring Expedition, Dr. Joseph Hooker, the eminent botanist, and Dr. Oldham, the Director of the Geological Survey of India, all of whom, however, pin their faith on my reverend friend's announcement that he has, in certain instances, obtained the spiriferæ, productæ, and other true carboniferous shells, from beds situated above those which contain the fossil plants in dispute.

" Were this one fact ascertained beyond the possibility of error, and proved not to be due to the accidental contortion or dislocation to which strata have sometimes been subjected, the question would be at an end ; and so desirable do I regard it for the progress of geological science especially in Australia and India, that it should be settled without loss of time, that, were our Government Geologist possessed of more leisure, I should long since have urged his being despatched to New South Wales to make a special investigation on the spot, as he formerly did in Tasmania, where he established the position of this same plant-bearing sandstone as being in every case above the clay in which the pachydomous shells are there embedded.

" Failing this, I am in hopes, from what Sir William Denison told me, of procuring a report on this subject from Mr. Keene, the inspector of coal fields in New South Wales, who is engaged in investigating the stratigraphical succession of these deposits.

" Meanwhile the controversy has been revived, and carried on with much ability on both sides, in consequence of the discovery, a few months ago, in our own Cape Patterson coal fields, of a fossil fern, of a kind called, from its fancied resemblance to a wreath, *Tœniopteris*, a genus classed by palæontologists among those typical of the Oolitic formation, so that its presence strengthens the previous inference as to our coal being of that age."

It will be interesting now briefly to set against this the field evidence submitted by Clarke ; evidence, however, apparently not convincing to McCoy and others.

As opportunity had offered during the period 1843–1861, Clarke had been examining the Stony Creek (Maitland or Greta) Coal Measures, with the idea of ascertaining their economic possibilities and their age. His report of 1861 (Clarke, 1861–64) shows the Maitland or Greta Coal Measures as forming a large anticline or dome, the measures being both overlain and underlain, conformably by marine beds, the upper marine beds in turn being succeeded conformably by the Newcastle Coal Measures. " On the north-west side of Harpur's Hill the dip of the beds (Maitland Measures) is reversed and falls in that direction towards Black Creek....No. 2 gives the horizontal section from Maitland to Anvil Creek, in which the coal seams of Stony Creek and of the falls to Black Creek are shown in reverse order, proving that they really belong to the succession of the beds in which they occur."

Clarke appears to have traced these lower coal measures for some miles both on the eastern and western slopes of Harpur's Hill.

In his mention of the organic remains he states that : " From West Maitland and two miles further (East Maitland) to about two and a half miles towards Lochinvar, the whole country is occupied by a succession of beds of sandstone, grit and calcareous concretionary rock, full of fossils of Palæozoic age, such as *Spirifers*, *Producti*, *Conulariæ*, *Orthoceratites*, *Asteriadæ*, *Pachydomi*, *Eurydesmæ*, *Fenestellæ*, *Bellerophon*, etc., which are exposed in the cuttings, and in quarries, and on surface blocks " (p. 28). He discusses the relation of the " Mulberring Creek " and the Muree " conglomerate " beds to the coal measures. His point about the Palæozoic age of the lower coal measures thus appears clear both from the text and from his section. Again quoting : " It will be seen from the above....that about Maitland, the Four Mile Creek and Greenhill coal seams of the Newcastle basin are separated from the Stony Creek coal by the Palæozoic fossiliferous beds.... for nearly twenty years I have been working out the details of the country in question...." (p. 30).

Incidentally he refers to the economic aspect. " The coal is partly cannel, partly splint, and soft coal. They appear to be about equal in gas ; the cannel burns to a white ash, the others to a brown ash. The specific gravity of the large seam I make 1.281. The coal in the corresponding seam on the north-west side of the anticlinal is nearly the same. The coal is worked on the dip for about thirty yards, and it is sold at the pit's mouth at 11s. a ton " (p. 31).

It is to be noted that Clarke referred to these coal measures and the associated marine beds as belonging to the Carboniferous. He does not refer to them as being Permian, not even in his 1866 and 1870 reports.

McCoy did not appear to have been convinced even by Clarke's clear statement of 1861, mentioned above, and he returns to the attack in his Presidential Address to the Royal Society of Victoria in 1864, wherein he stated that Daintree had endeavoured to compose the points in dispute between Clarke and himself concerning the geological age of the Newcastle coal, for Daintree's remarks had led him to consider that Clarke " in making his original collections for determination had mixed together the fossils of the upper and lower beds ". McCoy reported also that Keene was collecting the material " anew with scrupulous care ". The result of Keene's field work was announced in 1865. He considered the Coal Measures of Newcastle to be as old as those of the Palæozoic of Europe.

In 1866 Daintree and Wilkinson described the Bacchus Marsh tillite and considered it to be Carboniferous in age, but the influence of McCoy prevented general acceptance of their views.

In 1866 Clarke's field work enabled him to classify the coal measures and the associated marine rocks in descending order as :

Upper Coal Measures.
Upper Marine Beds.
Lower Coal Measures.
Lower Marine Beds (with Palæozoic plants).

In 1878 he placed the Hawkesbury beds in the Triassic.

In 1872 Daintree described Glossopteris and Phyllotheca with Palæozoic marine fossils in Queensland.

In 1880 Wilkinson, Government Geologist of New South Wales since 1873, applied the term Permian to the Upper Coal Measures and the term Carboniferous to the lower beds (*Ann. Rept. Dept. Mines*, 1879, p. 216). At this time he discovered glacial formations in the Upper Marine. About this time also he attempted a correlation of the coal exposed in the many prospecting pits dotting the Greta coal seam for miles. This correlation, he informs us, he effected by

means of the associated Greta Conglomerate which, by its resistant nature, provided a prominent outcrop. During the year 1884 he summed up his important work on the Greta Measures thus : " It will be seen that the Greta seams are the lowest of the series in this district, and that their present outcrop at the surface is due to the denudation of a great anticline caused by the irruption of the diorite near Lochinvar ".

Wilkinson, however, owing to the exigencies of routine administration, felt unable to complete the necessary field work on this highly important economic structure, and he entrusted T. W. E. David, Geological Surveyor, with the task of mapping the structure in detail. David's survey was begun about the end of May, 1886, and the results of his prospecting work—in the vicinity of a mass of loose coal blocks reported by Tester, a local resident—were so promising that by early July a reserve of 23,700 acres was made over the structure by the State Government, on Wilkinson's recommendation. This deviation into the field of economics appears justifiable because it is just the economic importance of the coal itself which has enabled us to gain so great a knowledge of the Permian period in Australia. These observations of Clarke, carried on by Wilkinson, and completed by David, dispelled all doubts as to the Upper Palæozoic age of the Coal Measures. David's detailed survey of the Hunter River coal field gave the world a magnificent picture of the Australian Permian.

The occurrence of beds containing *Rhacopteris*, *Lepidodendron* and associated Carboniferous plant remains beneath the Upper Marine division of the so-called Permian, however, raised the question as to the upper limit of the Carboniferous and the downward extension of the Permian. Etheridge, in 1880, had proposed to group the Queensland coal measures and associated marine beds—all of the same age as the Newcastle-Maitland beds—as Permo-Carboniferous, and in 1892 Jack and Etheridge (*Geology of Queensland*, p. 71) applied the term Permo-Carboniferous to the whole of the similar formations of New South Wales and Queensland.

At the beginning of David's survey of the Hunter Valley coal field, the coal measures and the associated marine beds were generally referred to, therefore, as the Permo-Carboniferous ; David's survey, however, suggested that a series of sediments, named the Lochinvar beds, constituted the basal portion of this group.

In 1914 the lower limit of the Lochinvar beds in the Hunter River Valley was accepted as the base of the Permo-Carboniferous in eastern Australia. David drew attention also to the term Permo-Carboniferous as being unnecessary, inasmuch as, in his opinion, the strata above the base of the Lochinvar beds should be included in the Permian.

Complexity here again entered into the problem. Wilkinson, by reason of his training in 1866, with Daintree, on the ancient glacial deposits of Victoria, had discovered, in 1884, evidences of glacial action in the Upper Marine bed of the Hunter River area. Oldham, Director of the Indian Geological Survey, had visited Australia in 1885, and not only had confirmed Wilkinson in his glacial determinations, but in addition had found an ice-scratched boulder in the formation. Evidences of glaciation were found also in the Lower Marine beds. It had seemed fairly easy to locate the lower limit of the Permian, but when Sussmilch reported the occurrence of glacial beds in formations containing plant fragments strongly suggestive of the northern hemisphere Culm flora, and when, somewhat later, W. R. Browne found a grand sequence of sediments—at Winder's Hill near Lochinvar—containing definite Carboniferous (Aneimites, etc.) plants overlying tillites and varves, but all underlying the Lower Marine formations, the vexed question of what was Permian and what Carboniferous was raised again, inasmuch as it appeared highly improbable that glacial beds should

be found in contiguous members of two great periods such as the Carboniferous and the Permian.

As the result of this discovery, David placed the dividing line between the Carboniferous and the Permian about 2,500 feet, stratigraphically, above the base of his earlier measurements. The base of the Permian, as thus defined, consisted of a coarse conglomerate containing abundant remains of *Eurydesma cordatum*.

David, however, in 1923, returned to his earlier classification, placing the separation of Permian from Carboniferous " at the point where, at Lochinvar, the soft shales of the Lower Marine Series (Permian) are replaced by the harder rocks of the Kuttung ". This conclusion was supported by the work of W. R. Browne and W. S. Dun, who in 1924 recorded *Eurydesma hobartense* from the Lochinvar beds, these in turn resting directly upon the Kuttung (Lower Carboniferous).

C. Schuchert, of the United States, proposed to solve the difficulty by raising the glacial beds from the Kuttung and placing them in the Permian. The acceptance of this suggestion, however, would have raised a still greater difficulty, namely an apparent confusion of the Culm and *Glossopteris* floras in Australia. A. B. Walkom, with his knowledge of the *Rhacopteris* and *Glossopteris-Gangamopteris* types, pointed out, in 1929, that he " from comparisons of the fossil floras ", placed the base of the Permian in the position originally suggested by David, that is at the base of the Lower Marine Series. Attention was also drawn by Walkom to a point needing careful consideration in matters such as those under discussion, namely " the greater importance of the first prominent appearance of a new flora (or fauna) in the determination of age than the presence of the last lingering representatives of an earlier one ".

In 1930 David proposed the name " Kamilaroi System " for the " strata in the type district of the Hunter from the top of the Newcastle (Upper) Coal Measures to the base of the Lochinvar glacial beds ".

Walkom's work indicates a lower Carboniferous age for the *Rhacopteris* beds with the Permian resting (directly on this lower Carboniferous).

Such is the present position of one aspect of the Permian problem. That portion of the problem dealing with the Permian geosyncline, the sources of the strata, the foreland and the folding is considered later, under 4.

2. Problems of Glaciation.

The glacial history of Australia possesses a peculiar interest. Australia itself contains no glaciers today, and only within very limited areas is it subject to snowfalls, nevertheless it apparently possesses an absolute wealth of glacial relics in formations belonging to periods as widely separated in time as the Upper Pre-Cambrian, the Carboniferous, the Permian, the Cretaceous and the Pleistocene. The grand Pre-Cambrian glacial deposits of Broken Hill are so spectacular as to have aroused the interest of Sturt as far back as 1844, and he was puzzled to afford any rational explanation of these, to him, extraordinary occurrences. Sturt's difficulty, however, was but natural, because fossil tills, up to that time, had not been recognised in any country. Indeed, belief in the existence of fossil tills or of ancient glacial periods would have been contrary to all accepted religious and geological traditions, as well as to all recognised principles of solar and terrestrial physics.

Glacial traces, in ancient sediments of Australia, were, however, recognised shortly after Louis Agassiz had explained the origin of the widespread Pleistocene till of Europe. In 1859 Selwyn—who had received an admirable training in field geology on the British Geological Survey and was consequently qualified to form a valuable opinion on glacial occurrences—recorded the existence of a

fine glaciated pavement in ancient rocks in South Australia, but he does not appear to have determined the age of the glacial activity producing this feature.

W. B. Clarke in 1860 had noted many signs of glacial action in Recent time in the Kosciusko region. The evidence relied on by him in his determination was the existence of perched blocks, morainic material, and so on. The still more obvious evidences of glacial action such as cirques, rock basins, spur cutting, aligned spur bases and associated forms were not known in his time to have been the result of ice action.

In 1866 Daintree and Wilkinson placed on record the evidence for the existence of ancient glacial deposits in Victoria containing many large erratics, together with "grooved pebbles". In their published note the age of the deposits is not stated definitely, but E. J. Dunn, in a written communication, informed the writer that Daintree, personally, was convinced of their Palæozoic (Permian) age but that the failure to convince McCoy led him, with Wilkinson, to the following compromise: "As the Lower Mesozoic age of these beds has been assumed by Professor McCoy on the European analogies of the only distinct fossil in them—*Gangamopteris longifolius*—and as *Glossopteris*, another Mesozoic type in Europe, has been found in New South Wales and northern Queensland distinctly associated with Carboniferous fossils, it may not be asking too much to suspend judgment in this case a little longer".

Ralph Tate, immediately after his appointment (1876) to the Chair of Geology in Adelaide, commenced to make field observations and already in 1877, among other important finds, he had detected a glaciated pavement, associated with glacial beds, at Hallet's Cove, South Australia. Selwyn's discovery of 1859, stated above, was at Inman Valley. Tate, however, even as late as 1893, appears to have considered his pavement to be of late Tertiary age, for he wrote of it: "We may congratulate ourselves that a Post-Miocene glacial period occupies an unassailable place in the geological history of Australia".

R. L. Jack in 1879 reported the existence of a Permian tillite in the Bowen River coal field of Queensland. This find aroused great interest, as it was considered a remarkable thing for great glacial deposits to be found in the tropics.

R. M. Johnston in 1884 described a Permian tillite from Tasmania, while C. S. Wilkinson in the same year described a glacial deposit in the Upper Marine Series of the Maitland district in New South Wales.

R. von Lendenfeldt in 1885 reported evidences of Recent glaciation on the Kosciusko Plateau of New South Wales. Apparently he had little or no knowledge of the fact that Clarke had announced a Pleistocene glaciation there twenty-five years earlier. In 1894 this region was visited by R. Helms, who, unaware probably of the work of Clarke and Lendenfeldt, published an account of the evidence there of glaciation in Recent time.

Another important stage was reached in 1893, when E. J. Dunn recognised Permian and Recent glacial deposits in association on the west coast of Tasmania.

In 1895 T. W. E. David summarised the observations to date on glacial action in Australia.

In 1899 a considerable number of ice-scratched pebbles were found in the Lower Marine of Maitland. About that time also splendid examples of scratched pebbles were obtained from the Permian of northern Tasmania.

In 1901 David and Pittman visited Kosciusko and confirmed the observations of the earlier workers between 1860 and 1900.

Then came the announcement of the occurrence of tillite in ancient rocks at Sturt's Gorge near Adelaide by W. Howchin. Howchin described the age as Lower Cambrian, but the general concensus of opinion today is that it is Upper Pre-Cambrian in age. About 1912 Mawson described other grand exposures of Pre-Cambrian tillites in the Broken Hill district. These, by the way, were the

deposits which had so strongly impressed Sturt by their appearance, but had baffled him in searching for an explanation of their origin in 1844.

In 1920 Sussmilch described the occurrence of glacial deposits, including varves, in the Carboniferous sediments in the Hunter River district of New South Wales.

A further advance was made when, in 1921, many traces of apparent Cretaceous glaciation were observed in the Lake Eyre region and when, in 1928, ice-scratched boulders of the Upper Pre-Cambrian tillite were found re-distributed by Cretaceous ice action north of Broken Hill and near the Queensland border.

3. The Physiographic Problem.

It would seem that, in all departments of scientific research, it is commonly the broad features which escape notice, or which fail to be comprehended until a vast amount of detailed information has been obtained dealing with matters pertaining to the subject but of subordinate importance. It is as though the grander features are missed until one takes a general, or bird's eye view, as it were, of any great subject. As a simple illustration, one may fail to see the name of a large map simply by approaching it closely in order to read the names of local or subordinate features. In the same way, such apparently simple facts as space, time, matter and life are among the most difficult subjects to comprehend. And geology itself has not escaped this handicap, for it is only the other day, so to speak, that the nature, origin and age of the main topographic features of any large territory have been understood to any degree at all approaching that which has attended the study of the rock structure, the mineral composition, ore genesis, palæontology and so on, within that territory.

It may help us to appreciate this difficulty in geology if we make an approach by considering the topography of the hinterland of the Sydney and Melbourne areas. These are not only the areas of greatest and densest population, but they are those also which have been settled the longest in Australia. As such it would be natural to expect that the origin and age of the main topographic features, in these two large populous and important districts, would have received closer attention and would have been perceived more readily than the complicated details of mineralogy, stratigraphy, buried structures and palæontology of the areas. Yet what are the facts? We have seen Bass hinting at the sub-structure of the Greater Sydney Coal Basin, even as far back as 1797, nevertheless on the other hand we have seen geologists practically to the present century entertaining the belief that the plateaux behind are as old as the rocks of which they are composed.

As a sample of this backwardness in physiographic perception, let us consider first the ideas held until recently concerning the nature and age of the hill forms constituting the hinterland of Melbourne. Even as late as 1907 one of the leaders of geological thought in Australia wrote: "The high bank to the west of Bacchus Marsh, 1,000 feet in height, up which the train climbs on its way from Melbourne to Ballarat, is one of the oldest, well-preserved valley walls in the world. It was carved out by river erosion in Silurian times. It was in existence before the material of which most of the Alps are built had been laid down in the seas of central Europe. It was old before the first bird or mammal, or reptile, had been born upon the earth. That old valley wall remained long hidden beneath sheets of sand, gravel and clay . . . It has again been protected by a cascade of molten lava that poured over its edge from the volcanoes of the plateau . . ."

Visiting geologists, from New South Wales, about the same time (1907) had considered the scarp, however, to be a monocline, interrupted by faults, and probably only late Pliocene in age at the most, seeing that the overlying Tertiary basalts appear to have been subjected to the activity which produced

the scarp. The dissection itself was considered to be due to closing Pliocene or to Pleistocene action. On the other hand some of the British delegates to the 1914 meeting of the British Association for the Advancement of Science in Australia preferred to accept the old traditional explanation, as quoted above, to the revolutionising idea of a closing Tertiary to Pleistocene age for the scarp. Fenner's later report was an excellent application of modern physiographical principles to this area, and it came as a wholesome corrective to the older outworn explanation.

The physiographical features of the Greater Sydney district may be taken as our second instance. This is a more intricate area to unravel than the Melbourne hinterland. Leaving Sydney as a centre, one may travel south or west, passing successively across belts of Wianamatta Shale, Hawkesbury Sandstone, Narrabeen Beds, Upper Coal Measures (Permian), Upper Marine, Devonian, Silurian and Ordovician sediments. Regarded from the physiographic viewpoint, however, one passes southward and westward over a continuous and ascending slope or surface of slight angular value—deeply trenched and dissected in places, interrupted by breaks and warps in others—for very many miles. A very interesting feature is that each of the main formations mentioned above appears successively to rise, and end insensibly, against this great coextensive surface. The casual traveller experiences great difficulty in attempting to determine where the Hawkesbury beds give place to Narrabeen and Narrabeen to Permian. Even during the present century, senior geologists were accustomed to maintain that this extensive and co-extensive surface marked the upper limit of a great plain of accumulation. This, however, was seen to be fallacious, inasmuch as the surface itself was continuous and co-extensive, whereas each great formation successively encountered in the widening ring of older formations was seen to be acutely transected by it and, moreover, the sections exposed in the profound ravines revealed the fact that the angular value of the surface slope, in the non-dissected portions of the plateau, was less than the dip of the successively transected strata.

Here then there is a grand surface cutting alike through Ordovician, Silurian, Devonian, Permian and Triassic formations. Evidently the activity which produced this surface must be younger than the great rock formations it transgresses, even the youngest of them, namely the Triassic. Moreover, Tertiary basalts had flooded the surface in its earlier stages of construction, and these basalts in turn have been worn down in great measure by the activity which has given the magnificent outlines to the vast plateau surface itself. A belief that this plateau, or upland plain, surface is a post-basaltic, probably a closing Tertiary, feature thus forced itself upon the attention of open-minded workers.

As observations were extended, the idea dawned gradually upon observers that the plateau areas of Sydney and Melbourne, and their hinterlands, represent the differential uplift of low-lying plain-like areas to which erosion had reduced the youngest or latest of the local mountain systems. It was seen that the actual age of the plateau surfaces was undoubtedly great, but that its geological age was certainly young, the uplift, although accomplished only in many stages, nevertheless falling apparently within very late Tertiary time. The amount of dissection which the plateau has suffered, as evidenced by the profound ravines traversing it, evoked feelings within us thus of respect, and even reverence, for the duration even of Pleistocene time. Consequently we now regard with profound veneration those much greater divisions of time which preceded the Pleistocene and the late Pliocene.

Here another point of great interest became manifest. The plateaux of New England and of the great southern tablelands of New South Wales, together with their continuation as the plateaux and high plains of Victoria, were noted to be portions merely of the one great surface or peneplain, of erosion which

extended throughout eastern Australia, including the Sydney and Melbourne areas mentioned above. There are workers still alive who can remember the familiar statements about Kosciusko, " the roof of Australia ", being one of the oldest mountains on the earth, and that the New England plateau was as old, approximately, as the folded rocks whose structures terminated abruptly against it. The writer has a lively recollection of a strong criticism which was directed, by an eminent senior in science, against a statement which he, the writer, had proposed to include in an official publication by the State Department of Mines on the Hillgrove Gold Field. The proposed inclusion to which strong objection was taken was that the valleys of the Macleay River were declared therein to be youthful, whereas according to the criticism they were in reality very old, even geologically, because of the immense depths of the ravines excavated by the Macleay headwaters, suggestive of the great age of the rocks in which the valleys, upstream of the cañon heads had been excavated.

The appreciation of this physiographic principle has enabled us to see that the whole block of eastern Australia has moved as a structural unit, as a great slowly-moving earth undulation with broad and rolling crest, one whose main axial direction has changed from time to time. Nevertheless, even with these great advances we are far from possessing complete knowledge of our physiographic problems. We have made a good beginning, but we know very little of the details of the long-drawn-out story of successive peneplanation, differential uplift, upland valley erosion, revivals of uplift, wanderings of major axes of uplift and ravine formation. On the other hand we have the satisfaction of knowing that we are moving forward and that already we are far ahead of the stage when men conceived the granitoids as being the earliest deposits from a very hot ocean, and the rocks possessing steep and vertical dips as being very early deposits also from the same scalding waters. We have even advanced far beyond a much later stage when the mountains were considered to be as old as the rocks of which they were composed.

We may conclude with one more illustration of our physiographic advance. For this we cite our advance in the comprehension of ice action. Louis Agassiz and Charpentier recognised the glacial origin of the Drift of Europe one hundred years ago, but the cirque, the rock basin, the over-deepened valley and so on were not recognised generally until very recent years. Indeed, these forms were cited by leaders of geological thought as actual evidences of the inefficiency of glaciers as erosive agents. The writer remembers, in 1909, being assured by one of the leading British geologists that one had only to visit Italy and Switzerland to note how glaciers stagnate just at the places where glacialists have postulated the maximum amount of erosion ! It is no wonder, therefore, that Clarke, Lendenfeldt and Helms overlooked the splendid evidence of glacial erosion on the Kosciusko Plateau in the existence of the cirques, the rock basins and the facetted rock spurs.

Australian physiography now looks forward to working out the age and the variable stages in the formation of the Eastralian and Westralian peneplains, the age and stages of formation in the excavation therein of the later peneplain or upland valley forms ; the age and cause of the differential and successive uplifting which resulted in the great Eastralian Plateau. The problem of the antecedence and superposition of streams also calls for solution.

4. The Building of Australia.

Australian geologists find themselves confronted by the question : Whence were derived the enormous thicknesses of Ordovician, Silurian and other sediments in Australia ? It seems evident that, in very great measure, they have been derived from the erosion of associated land masses. What then was the nature of the lands from which they were derived ? Were they mountain

ranges resulting from one elevation only? Were they subject to oft-repeated and fluctuating uplift, such as seems to have been the experience of existing mountain ranges? Were the axes of elevation of these feeding lands stable during recrudescences of uplift—assuming such to have occurred—or did they wander? What structural relations did the basins, which received the sediments, bear to the feeding lands themselves? If the main axes of the geanticlines wandered, did those also of the associated basins? What activities brought about the great variations in width and depth of individual formations such as those of the Palæozoic? In which direction did the great formations thin away or disappear? In which directions did the folding thrusts move? Have we indications of the existence of ancient forelands and borderlands in Australia?

These and many related questions press for answer today. The harvest is great, but the real workers are few. Australia is 3,000,000 square miles, approximately, in area, and probably not much more than one per cent. (30,000 square miles) has been surveyed geologically with the same amount of detail and accuracy as the 3,500 square miles mapped during the period 1854–1869 by Selwyn's survey. The utmost one can expect to accomplish today in the matter of generalisation is to assemble such isolated scraps of field information as are available and infer therefrom the location and nature of the Australian forelands, borderlands, geosynclines, geanticlines, deltas, directions of thrusting, and so on.

The result may well be philosophical rather than eminently scientific, because of the lack of detailed field observations. Nevertheless, it should form a valuable, even if very open and patchy, framework for the guidance of workers in the matter of principles at least.

As illustrations of the difficult problems ahead for Australian workers, it may be helpful to take first a passing glance at the Permian, then at Ordovician, Silurian and Devonian problems.

Permian. The historical notes on the recognition of the Permian and its vertical limits have already been considered; the remarks at this stage are confined to its areal extent and its structure. Geologists for many years have studied the great Permian formations of Australia with their peculiar *Glossopteris* and invertebrate contents, their coal measures, their spectacular glacial contents and other interesting characteristics.

It so happened that the earlier main attacks on the Permian problem were made in the northern portion of the Main Coal Province of New South Wales. Those who conducted the notable field work there included Clarke (1843–1870), Keene (1864–70), Wilkinson (1880–90) and David (1886–1934). From the field work of Clarke the Permian was seen to comprise four great divisions, all conformable, but representing alternating marine and terrestrial conditions. The trough receiving the Lower Marine was limited in length and width; the succeeding Greta Coal Measures, with its "conglomerate" beds overlapped the Marine in part, the coal seams themselves being discontinuous. The Upper Marine overlapped the Greta markedly, and the Upper Coal Measures transgressed the Upper Marine in turn definitely in places. Near Maitland the Permian beds are domed, but the excellent work of Jones suggests that the dome itself is a structure of long standing (Jones, 1939), inasmuch as the sediments appear to thicken with distance from it as a centre, suggesting that the dome itself had been growing during the deposition of the Permian. Some observers had pictured the sediments as being derived from a mountain range to the west and south-west, while post-Permian movements had been considered to be of a mild order only, affecting Permian and Triassic practically alike, and resulting in the formation of a simple basin structure with gentle dip, the uppermost coal formations thereby rising about 3,000 feet above sea level in a distance of sixty

miles to the west, 1,000 feet above sea level about forty miles to the south, and sinking to 3,000 feet below sea level at Sydney near the centre of the basin, the rise northwards being somewhat less than that to the south and west.

Another stage, however, in the Permian problem was reached about the year 1905, when marine fossils, found in New England—to the north of the Hunter Valley—were described as Permian forms. The field notes accompanying the collections indicated that the sediments from which the fossils had been obtained had suffered from strong folding and plutonic intrusive action. These field notes were not accepted generally for years apparently, because work in the classic area of the Permian had not permitted a picture to be formed there of folding and plutonic intrusive phenomena in the Permian. A compromise was reached later when the accuracy of the field notes was admitted, with the proviso, however, that these conditions applied only to a very small area. At a later stage, in the more eastern portions of Queensland—and particularly clearly stated by J. A. Reid—the Permian was observed to have been strongly folded and intruded; it was noted also that the folding phenomena appeared to die away in a westerly direction, such that the western, or marginal, formations had been gently warped only. Moreover, the arrangement, suppression and thinning of beds in the western exposures indicated that the sediments had been derived from an easterly source. The picture given by this later work was of a geosyncline, with mobile geanticline lying to the east, the more pronounced sinking action occurring near the geanticline, the foreland lying to the west. Marine and terrestrial conditions alternated; the geosyncline may well have been double, with a central as well as an eastern geanticline; folding was accompanied by plutonic intrusions with folding directed from the geanticline area; the folding affected the eastern Permian sediments strongly, the intensity of movement dying away towards the western foreland.

Upper Pre-Cambrian and Lower Palæozoic. Upper Pre-Cambrian rocks with sub-horizontal attitude are recorded over great areas of northern and south-western Australia. Formations of this age are widely spread over north Australia, whereas they occur as thin formations only on the northern portion of the great south-western block. These beds are neither horizontal nor uniformly dipping; they present rather a gently undulating appearance, suggesting the initiation only of folding. This phenomenon appears to be characteristic of so-called sub-horizontal formations generally. On the north Australian shield these gently undulating Upper Pre-Cambrian beds, together with others belonging to the Cambrian and Ordovician, overlie the ancient Pre-Cambrian unconformably. All three are conformable with each other, the whole presenting the general appearance of undisturbed strata. Cambrian and Ordovician with these negligible dips are not recorded from the great south-western block, except perhaps as narrow bands dying away rapidly to the south. Their arrangement is such as to suggest that they were deposited in areas of shallow marine flooding, the sea retreating to the east. This vast extent of sub-horizontal, or gently undulating sediments, however, is broken abruptly along two grand curves, namely the Kimberley Arc, extending with convexity directed southward, from Cambridge Gulf to King's Sound via the Ord and Fitzroy River drainages, and the Greater Macdonnell Ranges Arc and its natural extensions westerly.

In the Kimberley Arc the Upper Pre-Cambrian and the Cambrian are strongly folded, the folds dying away in gentle undulations on the ancient blocks or forelands around. In the great east and west sweep of the Macdonnell area, so well described by Madigan, the Upper Pre-Cambrian, the Cambrian, the Ordovician and the (?) Silurian have been strongly folded with a general grand east and west strike, the folds dying away towards the ancient resistant blocks north and south, especially south.

The whole arrangement of the sediments suggests a general retreat eastwards of marine conditions in Australia after Ordovician or Silurian time.

The Greater Broken Hill area as shown by Mawson, Tate, Howchin and others consists of an ancient shield overlain by Upper Pre-Cambrian and younger rocks, which have a peculiar interest when they are considered in connection with the sediments lying to the west and east. Thus the ancient rocks of the Mount Lofty and Flinders Ranges are overlaid by great thicknesses of Upper Pre-Cambrian and Lower Cambrian sediments, all highly folded but unassociated with later Palæozoics. To the east of Broken Hill and the Darling River, on the other hand, lies a great width of Silurian and Devonian sediments, many thousands of feet in thickness and all highly folded. In striking contrast with the attitude of these Palæozoics is that of the sediments overlying the foundation of Broken Hill area itself. Here Upper Pre-Cambrian rocks, gently undulating or only moderately folded, overlie portions of the ancient foundation, whereas, to the east, rocks of this age are highly folded, somewhat altered, and intruded by plutonics. On these again rest other formations of different ages, comprising a great extent of conglomerates, quartzites, sandstones and so on. No determinative fossils have been found in these rocks, but they are believed to belong to the early and middle Palæozoic.

To the east a low shield, comprising very great thicknesses of Silurian, Devonian, and possibly Ordovician rocks, extends approximately in a meridional direction for one hundred miles both north and south of Cobar. A metamorphosed complex, in which no fossils have been found, follows this closely to the east. The Silurian and Devonian formations of the low Cobar Shield contain a marked development of coarse conglomerates, grits, quartzites, indurated sandstones and slates. The coarser types occur especially in the Silurian. Beyond this shield again other considerable exposures of Silurian and Devonian occur. The Silurian (Upper) includes conglomerates, grits, quartzites, sandstones, slates and limestones. The Devonian contains abundant quartzites, coloured shales and volcanic rocks. Beyond these again, to the east, there is an extensive development of Upper Ordovician and Upper Silurian, the latter comprising extensive coralline limestone formations, sandstones, slates and shales, all strongly folded and overlain unconformably by Devonian quartzites, sandstones, shales and volcanic rocks. In some places the Upper Devonian sediments of this south-eastern portion of the State are folded somewhat markedly, whereas in other places they are only gently folded, the underlying Silurian appearing to have been stabilised at an earlier period.

Detailed mapping alone may be expected to furnish a reliable picture of Ordovician, Silurian and Devonian conditions in the eastern, central and western divisions of New South Wales. The peculiar rock associations found at Broken Hill definitely point to it as being a foreland ; the immense thicknesses and marked folding of the Palæozoic rocks of the Cobar Shield indicate the existence there of a mobile geosyncline, with deltas being formed therein, the feeding geanticline lying immediately to the east. The peculiar sediments of the more easterly Palæozoic formations suggest a mobile geanticline, meridionally disposed, in eastern New South Wales, while the character and attitude of the eastern Devonian formations suggest a relative stabilisation of the eastern Silurian area in pre-Devonian time.

In Victoria one notes a peculiar succession of events. The Lower Ordovician is of enormous width to the west of the meridian of Melbourne. Field observations indicate the existence of an ancient and contiguous massif to the west. The eastern portion of the State is occupied in great measure by the Upper Ordovician, with mere traces only of Lower Ordovician, while the area separating

the two grand Ordovician formations of the State—one in the east the other in the west—is occupied by a long central trough containing Lower, Middle and Upper Silurian sediments, probably as much as 20,000 feet in thickness. Ordovician and Silurian alike are strongly folded, while great areas of the Upper Ordovician, in the east, have been markedly metamorphosed.

Middle Devonian, definitely folded, occurs in the extreme east of Victoria. With this exception the State of Victoria, as well as the whole of Tasmania, do not appear to have participated in folding movements later than the Epi-Silurian.

Eastern New South Wales and Queensland exhibit other profoundly instructive features, one of the most interesting of these being that of the Permian, already alluded to briefly.

A distinct story of sedimentation and folding is recorded in the magnificent rock exposures of the peripheral area of Australia, extending almost uninterruptedly from the Lower Hunter Valley as far north as Lat. 16° S. Whereas the main mass of Australia west of this peripheral belt experienced only epeirogenetic movements after the Epi-Devonian activity, the peripheral belt in question indicates a long-continued succession of rising and sinking, of sedimentation and folding, from the beginning of the Lower Devonian at least until the close of the Permian.

The Devonian, Carboniferous and Permian sediments attained enormous thicknesses in a trough occupying the peripheral area mentioned above. This trough appears to have been divided into two sequent troughs at times. Thrustings from the east were strongly developed, especially during the Carboniferous and towards, as well as at, the close of the Permian. These sediments represent the removal, by erosion, of great mountain ranges, or of lands of great breadth, subject to elevation more or less frequently, for the total thickness recorded of Devonian, Carboniferous and Permian appears to have exceeded 50,000 feet. The arrangement and variable thickness of the sediments suggest that the feeding geanticline or geanticlines lay to the east and that deltas must have been formed. Folding activities appear to have died away, definitely, to the west.

Post-Palæozoic activities appear to be confined to undulating movements of an epeirogenic nature, allowing the alternation of shallow marine and terrestrial conditions, especially in eastern Australia. New Zealand, with New Guinea, and other islands belonging to the arc surrounding northern and eastern Australia, apparently absorbed in great measure the undulatory shocks which came from the Pacific direction during the Mesozoic and Tertiary.

It would seem that Australia, as seen today, represents the result of the welding together of several ancient blocks of land (Andrews, 1937) by a process involving the formation of troughs and complementary geanticlines, the folding of the trough sediments, and the action of thrusting which proceeded characteristically from the geanticlinal direction and towards the stable blocks or forelands. The more important of these troughs include that of the Kimberley, the Macdonnell—with its earlier extension towards the Indian Ocean via the Oakover or neighbouring areas—the Flinders, the Ordovician and Silurian basins of Victoria, the Ordovician, Silurian and Devonian basins of southern and central New South Wales, with the Pre-Devonian, Devonian, Carboniferous and Permian basins occupying the peripheral area of New South Wales and Queensland between Lat. 33° S. and Lat. 16° S. The borderlands and geanticlines which furnished the enormous supplies of sediments through successive geological ages appear to have disappeared almost entirely.

Later mapping will furnish material for a fuller and more accurate picture of Australian growth, but the work of the pioneers is of value sufficient to indicate the advance summarised in this note.

Acknowledgments.

Where the assistance, from so many sources, has been so great, it would be difficult to make adequate acknowledgment, but I wish especially to mention the assistance received from the excellent summary of the history of geological research in Australia, by R. Tate in his Presidential Address to the Adelaide meeting (1893) of the Australian Association for the Advancement of Science.

My cordial thanks are due also to my colleague, H. G. Raggatt, for notes on the history of the State Geological Surveys, and to the late E. J. Dunn for valuable personal communications on the work and personalities of Selwyn and the senior members of his Victorian staff.

References.

Andrews, E. C., 1937. Structural History of Australia during the Palæozoic. This Journal, **71**, 118–137.

Barkly, H., 1861. Pres. Add. Roy. Soc. Vic.

Clarke, W. B., 1861–64. Coal Seams near Stony Creek, West Maitland District. *Trans. Roy. Soc. Vic.*, 27–31, with field sections.

Jones, L. J., 1939. Coal Resources....Maitland....Coal District. *Min. Resources* No. 37. Dept. Mines, N.S.Wales, 169–173.

Tate, R., 1893. Pres. Add. Aus. Assoc. Adv. Sci., Adelaide.

THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

Part IV. Polynuclear Complexes of Rhodium and Tin with Tertiary Arsines.

By F. P. Dwyer, M.Sc.,
and R. S. Nyholm, B.Sc.

Manuscript received, April 14, 1942. Read, June 3, 1942.

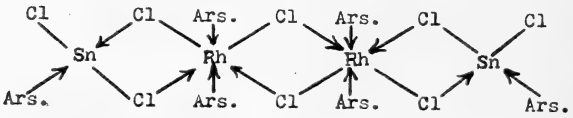
In a previous paper (Dwyer and Nyholm, 1941), reference was made to the isolation of a compound $RhCl_2 . SnCl_2 . 3Ph_2AsMe$ by the addition of the arsine to rhodous salt solutions that had been reduced with stannous chloride. Compounds of this general type are especially interesting in view of the recent isolation of bridged metallic complexes containing two different metallic atoms such as mercury and cadmium, or palladium and mercury (Mann and Purdie, 1940).

The rhodous compounds have now been investigated in detail in order to ascertain the function of the tin atom in the complex, and also to determine whether the usual coordination number of six for bivalent rhodium is operative. For comparative purposes a number of rhodic complexes have also been prepared. In all cases the compounds proved difficult to work with owing to the ease of elimination of the stannous halide. Indeed, owing to this fact, whereas the chloride compounds were ultimately isolated in a state of purity, the bromide and iodide compounds existed only in solution in the presence of excess stannous halide. Owing to dissociation into lower molecular weight fragments in solution, the molecular weights of all compounds were abnormally low, and the formulæ assigned to them are based upon the assumption that the usual coordination numbers of four and six are operative for tin and rhodium respectively. In one case, however, a satisfactory formulation required the tin to be six covalent.

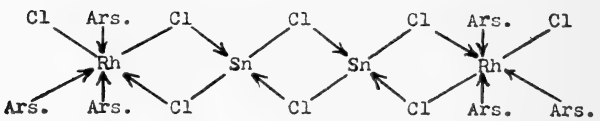
With diphenylmethylarsine two different complexes of the same empirical formulæ, $RhCl_2 . SnCl_2 . 3Ph_2AsMe$, were isolated ; compound (I) was prepared by the direct addition of stannous chloride to tris-diphenylmethylarsine rhodous chloride $(RhCl_2 . 3Ph_2AsMe)_2$. In view of the pronounced stability of these rhodous halide arsine complexes it is considered that the halogen bridge between the two rhodium atoms remained intact and two tin atoms were attached at the ends of the molecule. The second compound (II) was prepared by the addition of the arsine to a solution of rhodous chloride containing excess of stannous chloride. Assuming that (I) and (II) are isomeric, it would appear that (II) could be formulated as (IIa) or (IIb). There does not appear to be any simple method of distinguishing between these alternatives but (IIa) appears the more likely from considerations of symmetry. Both compounds were essentially covalent in nature, being extremely soluble in organic media and insoluble in water.

With rhodic chloride two different types of compound (III) and (IV) were isolated, using p-tolyldimethylarsine and diphenylmethylarsine respectively. Apparently dialkyl arsines tend to form compounds of type (III) exclusively, and diaryl arsines compounds of type (IV), since under no conditions of variation of the relative amounts of the constituents could any other compound than (III) be obtained with p-tolyldimethylarsine, or than (IV) with diphenylmethyl-

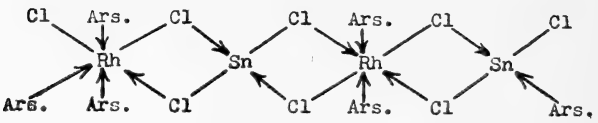
arsine. Like the rhodous compounds they were extensively dissociated in solution, and by successive crystallisation from alcohol the previously described tris arsine rhodic chlorides were easily isolated in the pure state. The compounds could be crystallised unchanged from alcohol in the presence of excess stannous chloride provided that the operation was performed rapidly in order to avoid reduction of the trivalent rhodium.



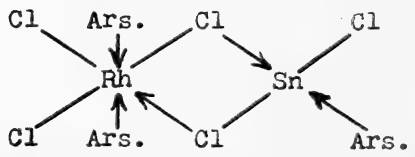
(I)



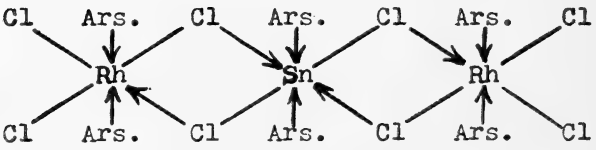
(IIa)



(IIb)



(III)



(IV)

Experimental.

Dichloro - hexakisdiphenylmethylarsine - μ - dichloro - tin - rhodium^{II} *- μ - dichloro - dirhodium*^{II} *- μ-dichloro-rhodium*^{II}*-tin* (*I*). Tris-diphenylmethylarsine rhodous chloride, 0·3 g., was suspended in alcohol (100 mls.), stannous chloride (1 g.) was added, followed by concentrated hydrochloric acid (0·5 mls.), and the mixture refluxed. The brown crystals of the rhodous compound gradually dissolved to an orange solution, which was filtered whilst hot and the filtrate cooled. On the

addition of water a yellow amorphous precipitate came down. After filtration this was washed with aqueous alcohol, then dilute hydrochloric acid and finally much water. The substance became brown at 147° and melted at 149°. It was readily soluble in alcohol, acetone, and benzene from this latter solvent it was easily precipitated with petroleum ether.

Found: Rh, 9·55%; Sn, 10·3%; Cl, 12·97%.
Calculated for $(RhCl_2 . SnCl_2 . 3Ph_2AsMe)_2$: Rh, 9·39%; Sn, 10·86%; Cl, 12·96%.

Dichloro - hexakisdiphenylmethylarsine - μ - dichlororhodium^{II} *- tin - μ - dichloro - di - tin - μ - dichloro-tin-rhodium*^{II} (*II*). Rhodium trichloride solution (10 mls.) containing 0·093 g. rhodium was treated with sodium hydroxide in excess to form sodium rhodite, and a solution of sodium stannite prepared from 2·5 g. of stannous chloride added. The black precipitate of hydrated rhodous oxide which formed on boiling was then dissolved in sufficient concentrated hydrochloric acid. The dark red solution of rhodous chloride was then added to a solution of diphenylmethylarsine (0·9 g.) in alcohol (50 mls.) and concentrated hydrochloric acid (10 mls.). The mixture after refluxing for about thirty minutes was filtered from a small amount of black substance, and on the addition of water and cooling gave a yellow microcrystalline powder, m.p. 129°. As mentioned previously, molecular weight determinations with both of the above complexes was unsatisfactory due to decomposition in the benzene. This decomposition was most pronounced with this latter compound; stannous chloride gradually precipitated and the solution developed a pronounced odour of arsine.

Found: Rh, 9·54%; Sn, 10·9%; Cl, 13·03%; mol. wt. in benzene cryoscopic, 805.
Calculated for $(RhCl_2 . SnCl_2 . 3Ph_2AsMe)_2$: Rh, 9·39%; Sn, 10·86%; Cl, 12·96%; mol. wt., 2,190.

Dichloro-tris-p-tolyldimethylarsine-μ-dichlororhodium^{III}*-tin* (*III*). Rhodium trichloride (10 mls.) containing 0·078 g. rhodium was treated with p-tolyldimethylarsine (0·5 g.) and hydrochloric acid 5N (1 ml.), and a clear solution brought about by the addition of alcohol (45 mls.). The solution was heated to boiling and a solution of stannous chloride (5 g.) dissolved in alcohol (10 mls.) added. The mixture was refluxed for five minutes, cooled, and a little water added until precipitation commenced. The solution was then reheated, about 20% of the alcohol evaporated off, and cooled. The yellow precipitate of rounded needles melted at 111° C. The compound could be crystallised from alcohol in the presence of stannous chloride, but dissociated in all solvents in the absence of tin salts.

Found: Rh, 10·96%; Sn, 17·9%; Cl, 12·4%.
Calculated for $RhCl_3 . SnCl_2 . 3Tol . AsMe_2$: Rh, 10·68%; Sn, 17·9%; Cl, 12·02%.

Tetrachloro - hexakis - diphenylmethylarsine - μ - dichlororhodium^{III} *- tin - μ - dichloro - tin - rhodium*^{III} (*IV*). Prepared in the same manner as compound (III) above, this gave a yellow microcrystalline powder, m.p. 169° C. On heating with alcohol the substance became gummy, but ultimately dissolved to a yellow solution, which on cooling deposited a mixture of yellow rhombs and an amorphous powder. Recrystallisation of this product gave orange yellow crystals, m.p. 176–178°, which was identified as the insoluble form of tris-diphenylmethylarsine rhodic chloride (Dwyer and Nyholm, 1941*b*). The soluble form of the same compound was obtained from the benzene solution used in an attempt to determine the molecular weight of tris-diphenylmethylarsine-stannous-rhodic chloride, $(RhCl_3 . 3Ph_2AsMe)_2 . SnCl_2$.

A great many attempts were made to prepare a compound corresponding to (III) above, i.e. $RhCl_3 . SnCl_2 . 3Ph_2AsMe$, such as using a great excess of stannous chloride in the preparation, or recrystallising the compound from a saturated solution of stannous chloride. In all cases the same compound $(RhCl_3 . 3Ph_2AsMe)_2 . SnCl_2$ was obtained. The pronounced dissociation of the compound in solution in the absence of stannous chloride, and the isolation of tris-diphenylmethylarsine rhodic chloride from such solutions suggests that the required analogue of (III) is probably formed by dissociation, but efforts to isolate it have been unavailing.

$$(RhCl_3 . 3Ph_2AsMe)_2 . SnCl_2 \longrightarrow RhCl_3 . 3Ph_2AsMe + RhCl_3 . SnCl_2 . 3Ph_2AsMe.$$

Found: Rh, 10·0%; Sn, 6·4%; Cl, 13·6%; mol. wt. cryoscopic in benzene, 961.
Calculated for $RhCl_3 . 3Ph_2AsMe)_2 . SnCl_2$: Rh, 9·98%; Sn, 5·73%; Cl, 13·74%; mol. wt., 2,072.

Analysis. The analysis for the halogen was carried out by the distillation of 0·1 g. of the substance with concentrated sulphuric acid, and collecting the evolved halogen acid in standard silver nitrate. Rhodium and tin were estimated by fuming approximately 0·2 g. of the substance with concentrated sulphuric acid to remove the halogen and avoid loss of tin as the volatile stannic chloride. Solid potassium nitrate was then added, and the heating continued until all of the organic matter was destroyed, and the residue evaporated to dryness. It was then treated with 50 mls. of distilled water and boiled to hydrolyse the stannic salts. The resulting white precipitate of stannic oxide, basic stannic sulphate and basic stannic arsenate, was dissolved, after filtering, in hydrochloric acid 5N and gently boiled with 30% hypophosphorous acid. The brown precipitate of arsenic was removed from the stannous chloride and excess reducing agent. The excess of the latter was destroyed with iodine, and the tin, after reduction with nickel shot, was titrated with iodine. The rhodium was estimated in the filtrate from the original tin precipitate by reduction with alkaline hydrazine, followed by ignition in a reducing atmosphere.

References.

Dwyer, F. P., and R. S. Nyholm, 1941*a*. This Journal, **75**, 127.
———————————, 1941*b*. *Ibid.*, **75**, 75, 140.
Mann, F. G., and J. S. Purdie, 1940. *J. chem. Soc.*, 1230.

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CONTENTS

VOLUME LXXVI

Part III

Page.

ART. X.—The Chemistry of Bivalent and Trivalent Rhodium. Part V. Coordination Complexes of Rhodous Halides with Dialkyl Arsines. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued December 21, 1942) 133

ART. XI.—The Effect of Gonadotropin Obtained from Human Pregnancy Urine on the Pouch of *Trichosurus vulpecula*. By Adolph Bolliger, Ph.D. (Issued December 21, 1942) 137

ART. XII.—The Devonian Rugose Corals of the Tamworth District, N.S.W. By Dorothy Hill, Ph.D., D.Sc. (Issued December 21, 1942) 142

ART. XIII.—The Tamworth Series (Lower and Middle Devonian) near Attunga, N.S.W By Ida A. Brown, D.Sc. (Issued December 21, 1942) 165

ART. XIV.—On Contact Transformations Associated with the Symplectic Group. By H. Schwerdtfeger. (Communicated by Professor H. S. Carslaw.) (Issued December 21, 1942) 177

ART. XV.—Middle Palæozoic Rugose Corals from the Wellington District, N.S.W. By Dorothy Hill, Ph.D., D.Sc. (Issued December 21, 1942) 182

ART. XVI.—Some Thermochemical Properties of the Torbanite of the Glen Davis Deposit. By R. F. Cane, M.Sc., A.A.C.I. (Issued December 21, 1942) 190

ART. XVII.—Moving Sources of Heat and the Temperature at Sliding Contacts. By J. C. Jaeger. (Issued April 2, 1943) 203

ART. XVIII.—A Method for the Estimation of Vegetable Material in Scoured Wool. By M. Lipson, B.Sc., A.A.C.I. (Issued April 2, 1943) 225

THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

Part V. Coordination Complexes of Rhodous Halides with Dialkyl Arsines.

By F. P. Dwyer, M.Sc.,
and R. S. Nyholm, M.Sc.

Manuscript received, July 8, 1942. Read, August 5, 1942.

In a previous paper (Dwyer and Nyholm, 1941*a*) dimeric complexes of rhodous halides with diphenylmethylarsine of the general type $(RhX_2 . 3AsR_3)_2$ were described, in which the six covalency of bivalent rhodium was maintained by a halogen bridge. The close relationship between cobalt and rhodium in the trivalent state suggests a similarity in the bivalent state, in which cobalt, although generally hexacovalent, frequently yields tetracovalent derivatives such as bis salicylaldoxime cobalt (Mellor and Craig, 1940). By using tertiary arsines as the coordinating groups, this expectation has not been realised with rhodous salts, which persistently exhibit the higher coordination number. In a series of experiments with this object in view, with rhodic chloride and three, two, one and one-half mole of diphenylmethyl arsine, the same compound was isolated in each case, the lower ratios of arsine merely reducing the yield of $(RhCl_2 . 3Ph_2AsMe)_2$.

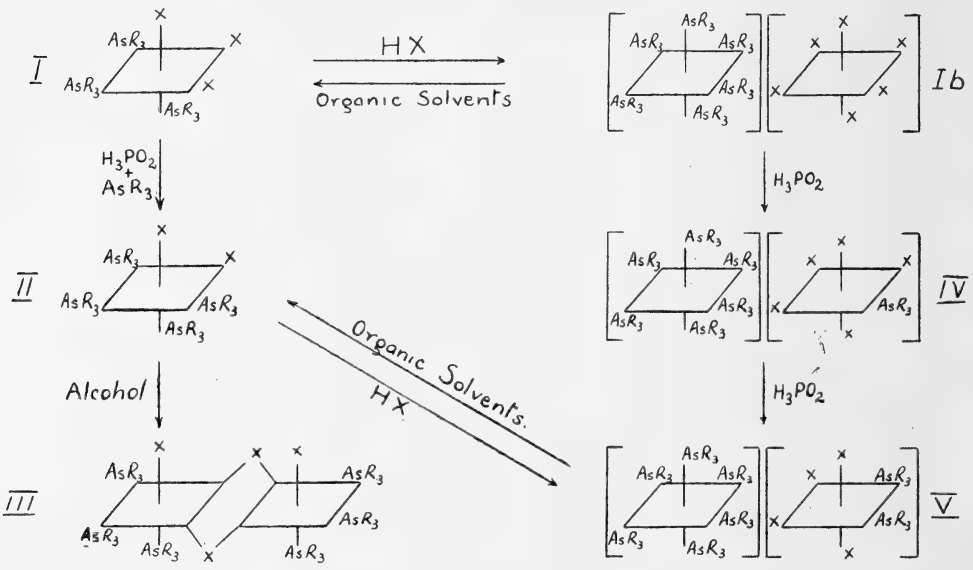
With the dialkyl arsines dimethylphenylarsine, and dimethyl-p-tolylarsine, however, a new type of monomeric covalent complex $RhX_2 . 4AsR_3$ has been isolated. The new complexes were extremely soluble in organic solvents, and even in petroleum ether; all were pale yellow in colour. They gave no precipitate of the silver halide with cold alcoholic silver nitrate, whilst on heating a violet to purple colloidal suspension of silver formed, followed later by the precipitate of the silver halide. In some cases this reaction yielded a silver mirror. Like the compounds previously described, the new compounds were prepared by the reduction of the rhodic compounds formed *in situ* with hypophosphorous acid. It might be mentioned that this is a general type of reaction and is at present being used for the preparation of the pyridine and ethylene-diamine coordinated complexes.

As a result of this study it is now possible to indicate the probable mode of formation of the various rhodous arsine complexes, and at the same time the persistence with which the hexacovalency of the rhodium atom is maintained.

The rhodic complex (Dwyer and Nyholm, 1941*b*) (I) which exists also in a salt-like dimeride (I*b*), has one halogen atom removed by the reducing agent, and the vacant coordination position is filled with one molecule of arsine to yield the tetrakis arsine compound (II). In solution in (preferably) aqueous alcohol (II) is partly dissociated, and provided the solubility relationships are suitable, one arsine atom is lost, the vacant coordination position is filled by a halogen bridge, and compound (III) is precipitated. This transition has been observed in two instances, and the reverse reaction apparently is possible also, since compounds of type (III) which are normally insoluble in alcohol, can be dissolved in alcohol containing arsine. The tetrakis compound (II) should be capable of existing in cis and trans forms, but owing to the ease of oxidation of the iodide, and the ease of elimination of arsine to form compounds of type (III)

with the bromide and chloride, one form only, probably the trans, has been isolated.

The red salt-like dimeride (*Ib*) is reduced to the mixed red rhodous-rhodic complex (IV), then into the red rhodous salt-like dimeride (V), which like the parent dimeride (*Ib*) is transformed into the yellow monomeric tetrakis compound (II) by solution in hot organic solvents. This latter series of transformations is not so well established, since it is extremely difficult to stop the reduction at the stage of the compound (IV), or to prevent compound (V) rearranging to (II). Out of a great number of experiments only two pure specimens of compound (IV)



were isolated, and the amounts were insufficient for molecular weight determinations. Generally, mixtures were isolated, and the rhodium halogen ratio varied from 1 : 2·2 to 1 : 2·8. The salt-like rhodous compound (V) was obtained pure with dimethylphenylarsine, but only an impure specimen with dimethyl-*p*-tolylarsine. The transformation from the monomeric compound (II) to (V) could, to some extent, be effected by boiling with halogen acid in the presence of hypophosphorous acid, but the reaction proceeds only on the surface and cannot be brought to completion.

The stability of the rhodous arsine complexes towards oxidation is least with the iodide and greatest with the chloride, whilst the tris arsine dimerides are more stable than the tetrakis monomers. The tendency to form the tetrakis compounds is greatest with the iodides, which eliminate one molecule of arsine with difficulty, whilst the chlorides pass to the tris arsine compounds merely by rubbing with a small amount of petroleum ether.

Experimental.

Tetrakis-Dimethylphenylarsine Rhodous Iodide (*II*). Rhodium trichloride solution (10 mls.) containing 0·097 g. of rhodium was treated with 0·8 g. of dimethylphenylarsine, hypophosphorus acid (30%), 3 mls., hydriodic acid (57%), 10 mls., previously reduced with hypophosphorous acid, and sufficient alcohol added to produce one phase. The solution became dark red and precipitated a reddish substance, which slowly dissolved, on continued refluxing in an atmosphere of carbon dioxide. The reaction was stopped when the solution had become a pale yellow colour, and the solution cooled in carbon dioxide. The yellow microcrystalline precipitate was filtered

and washed with 50% alcohol and dried rapidly. It slowly darkened on keeping owing to oxidation, and melted at 79–80° C. An alcoholic solution precipitated no silver iodide from cold alcoholic silver nitrate, but on boiling gave a colloidal suspension of silver, followed later by a precipitate of silver iodide. The compound was extremely soluble in acetone, benzene, and even in petroleum ether.

Found: Rh=9·83%; I=23·59%.

Calculated for $RhI_2 . 4((CH_3)_2 . As . (C_6H_5))$: Rh=9·49%; I=23·41%.

Tetrakis-Dimethyl-p-tolylarsine Rhodous Iodide II. Prepared in a similar manner to the compound above using dimethyl-p-tolylarsine, this gave an orange-yellow crystalline powder, m.p. 80–82° C.

Found: Rh=9·25%; I=22·26%; mol. wt. in benzene cryoscopically=975.

Calculated for $RhI_2 . 4((CH_3)_2 . As . (C_6H_4CH_3))$: Rh=9·02%; I=22·28%; mol. wt.=1141.

Tetrakis-dimethylphenylarsine Rhodous Bromide II. Prepared in the same manner as the compounds above using pure rhodic bromide, the solution was refluxed until it became almost colourless, and then cooled in ice in the presence of carbon dioxide. The pale yellow, extremely soluble compound was precipitated as an oil, which became crystalline on standing in the refrigerator. In alcoholic solution it gave a silver mirror with silver nitrate on heating, and melted at 68–69° C. The compound was somewhat unstable and smelt strongly of arsine.

Found: Rh=10·18%.

Calculated for $RhBr_2 . 4((CH_3)_2 . As . (C_6H_5))$: Rh=10·21%.

Tetrakis-Dimethyl-p-tolylarsine Rhodous Bromide II. This compound precipitated as an oil which crystallised on cooling to a pale yellow microcrystalline powder, m.p. 68–70° C. The compound was extremely soluble in organic solvents, and became orange on keeping, due to oxidation.

Found: Rh=9·72%; Br=15·43%.

Calculated for $RhBr_2 . 4((CH_3)_2 . As . (C_6H_4CH_3))$: Rh=9·82%; Br=15·28%.

Tetrakis-Dimethylphenylarsine Rhodous Chloride II. Prepared in the usual manner, this gave an almost colourless oil which solidified at about −10° C., but immediately liquefied on removing from the freezing bath. No analyses thus could be undertaken, but the compound was extremely soluble in organic solvents, reduced alcoholic silver nitrate to the metal, but gave no precipitate of the silver halide except on continued heating. On warming with a deficiency of petroleum ether the compound dissolved and then crystallised out as a yellow powder, m.p. 88° C. This compound had only three molecules of arsine and proved to be the dimeride dichloro-hexakis-dimethylphenylarsine μ dichloro-dirhodium (III).

Found: Rh=14·10%.

Calculated for $(RhCl_2 . 3((CH_3)_2 . As . (C_6H_5))_2$: Rh=14·28%.

(The tetrakis compound requires Rh=11·40%.)

Tetrakis-Dimethyl-p-tolylarsine Rhodous Chloride II. Like the dimethylphenylarsine compound above, this formed an oil of low melting point, which by treatment with petroleum ether gave the lemon-yellow tris compound—$(RhCl_2 . 3((CH_3)_2 . As . (C_6H_5))_2$ (III). This latter compound melted at 87–88° C.

Found: Rh=13·8%.

Calculated for $(RhCl_2 . 3((CH_3)_2As(C_6H_5)))_2$: Rh=13·5%.

(The tetrakis compound requires Rh=10·75%.)

Hexakis-Dimethyl-p-tolylarsinerhodous pentaiodo mono-dimethyl-p-tolylarsine rhodite (IV). Rhodium trichloride solution (15 mls.) containing 0·12 g. rhodium was treated with hydriodic acid (57%), 20 mls., just decolorised with hypophosphorous acid, dimethyl-p-tolylarsine (0·65 g.) and refluxed for five minutes to form the rhodic iodide arsine complex. Hypophosphorous acid was then added to the red solution, and the refluxing continued for about thirty minutes, when a red precipitate came down and commenced to redissolve. The solution was filtered hot, and the brilliant red leaflets and needles washed with aqueous alcohol and then water. The

compound was sparingly soluble in alcohol, and organic solvents, but reduced alcoholic silver nitrate on heating. Examined under the microscope the substance proved to be homogeneous. The compound melted at 207° C.

Found: Rh=9·65%; I=28·83%.

Calculated for $(Rh((CH_3)_2As(C_6H_4CH_3)_6).(RhI_5.(CH_3)_2As(C_6H_4CH_3))$: Rh=9·74%; I=28·69%.

Attempts to prepare the corresponding bromide and chloride were fruitless. It will be evident that the preparative procedure described involves the formation and half reduction of the rhodic dimeride, which in the cases of the more soluble diakyl arsines, as has been demonstrated previously, can be prepared with iodides only.

Hexakis-dimethylphenylarsine rhodous pentaiodo mono-dimethylphenylarsine rhodite (*IV*). Attempts to prepare this compound by the same method as the dimethyl-p-tolylarsine compound above always yielded an impure product consisting of mixtures of hexakis-dimethylphenylarsine rhodic hexaiodo rhodite (I*b*) and the required compound, indicating that the solubility relationships between the two compounds were unsuitable. This is evident by the analytical results.

Found: (1) Rh=10·2%; I=34·4%; Rh : I=1 : 2·73. (2) Rh=10·6%; I=36·4%; Rh : I=1 : 2·78. (3) Rh=9·93%; I=34·8%; Rh : I=1 : 2·84.

Calculated for $(Rh((CH_3)_2AsC_6H_5)_6).(RhI_5.(CH_3)_2AsC_6H_5))$: Rh=9·81%; I=30·2%; Rh : I=1 : 2·5.

Hexakis-dimethylphenylarsine rhodous tetraiodo bis-dimethylphenylarsine hyporhodite (*V*). Rhodium trichloride solution (10 mls.) containing 0·092 g. rhodium was treated with potassium iodide, 0·5 g., and dimethylphenylarsine, 0·5 g. (3 mols.). Acetone was then added in sufficient quantity to produce one phase, and the solution refluxed for a short time to produce the rhodic compound probably as a mixture of the two forms (I) and (I*b*). The orange solution was then treated with hydriodic acid (10 mls. of 57%), to transform the monomeric form (I) to the dimeride (I*b*), and hypophosphorous acid, 3 mls. The mixture was refluxed for a further two hours in the presence of carbon dioxide, when it became deep red and deposited a small amount of dark coloured precipitate. There was no tendency to lighten in colour on continued boiling (compare with preparation of the monomeric tetrakis compound above). After filtering, the solution was cooled in carbon dioxide, when it deposited brilliant purplish red twinned needles, which were recrystallised from cold acetone in the presence of hydriodic and hypophosphorous acids by the addition of water. The compound melted sharply at 210° C. Molecular weight determinations could not be undertaken owing to the ease of oxidation in solution in the absence of hypophosphorous acid, and the tendency to revert to the monomeric tetrakis compound (II) in the absence of halogen acid. The compound could be prepared in an impure form by boiling the yellow tetrakis compound (II) with concentrated hydriodic acid in the presence of hypophosphorous acid, when it became red in colour, and the melting point gradually rose.

Found: Rh=9·77%; I=23·40%.

Calculated for $(Rh((CH_3)_2As(C_6H_5))_6).(RhI_4.2((CH_3)_2As(C_6H_5)))$: Rh=9·49%; I=23·41%.

Acknowledgment.

The authors' thanks are due to Mr. D. Ford for assistance in the preparation of some of the above compounds.

References.

Dwyer, F. P., and Nyholm, R. S., 1941*a*. This Journal, **75**, 129.

Dwyer, F. P., and Nyholm, R. S., 1941*b*. This Journal, **75**, 140.

Mellor, D. P., and Craig, D. P., 1940. This Journal, **74**, 495.

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THE EFFECT OF GONADOTROPIN OBTAINED FROM HUMAN PREGNANCY URINE ON THE POUCH OF *TRICHOSURUS VULPECULA*.

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(From the Gorbon Craig Research Laboratory, Department of Surgery, University of Sydney.)

With Plate I and one text-figure.

Manuscript received, July 15, 1942. Read, August 5, 1942.

Previously it has been shown that œstrogens (Bolliger and Carrodus, 1940*a* ; Bolliger and Canny, 1941) bring on a contraction of the pouch of the common Australian phalanger or possum (*Trichosurus vulpecula*), and that progesterone (Bolliger and Carrodus, 1940*b*) after a preliminary and comparatively small enlargement brings on a relaxation of this organ. There, however, still remained unanswered the question as to whether any of the other known sex hormones are capable of bringing on an expansion of the pouch comparable to that seen shortly before or during pregnancy in preparation for the entry of the young into the pouch and in pseudopregnancy (Bolliger and Carrodus, 1940*a*). For this reason the action of gonadotropic substances was examined. Of the two gonadotropins at my disposal, viz. the one obtained from human pregnancy urine and the one prepared from pregnant mare serum, it was found that the latter brought on a marked contraction of the pouch, followed by a doubtful enlargement. The product obtained from human pregnancy urine also produced an initial contraction of short duration, which, however, was then followed by a very marked enlargement of the pouch. Consequently the action of this hormone was more fully investigated.

TECHNIQUE.

Intramuscular injections each of 100 to 500 I.U. of gonadotropin obtained from human pregnancy urine (Gonan B.D.H.) were given to fully grown female possums. Most of the animals were injected three times and the three injections were given at three, four or seven day intervals.

Before, during and after the period of injections the interior of the pouch was frequently examined by putting a finger into it to ascertain its dimensions and its conditions such as moisture and its colour. The mammary glands were also palpated and their size ascertained. For visual examination, the lips of the pouch were lifted by means of a small retractor and in the case of a large pouch it was found advantageous to illuminate the interior with a head lamp. To gain some information about the potential capacity of the caudal half of the pouch where the mammary glands are and where consequently a pouch young will be situated, water was injected into it from a syringe which had a short, pliable piece of rubber tubing attached to its nozzle. For this test, which one may call the " pouch capacity test ", the animal was held by an assistant in a vertical position by its neck and tail. A second assistant held the hind legs of the animal. Then the rubber tubing connected to the syringe was introduced through the lips and pushed downwards till the caudal end of the pouch was reached. Warm water (approximately 35° C.) was then injected slowly till it began to flow out from the caudal end of the pouch-opening and the number of mls. injected were noted. This test gave valuable information about the capacity of the caudal and larger half of the pouch, in addition to its depth and width as ascertained by introducing

one's finger. Struggling of the animal, of course, interferes with the test, but in the majority of examinations and particularly in those cases where a large pouch was present, the animal rather seemed to like the introduction of warm water.

Findings.

In all the seven fully-grown females of varying ages and breeding-history injected with gonadotropin from human pregnancy urine, a typical response, though varying in extent, was noted.

Most dramatic results were obtained from reproducing females which recently had housed a pouch young and where the injections were started before complete involution of the pouch had taken place. A few days after the first injection was given the pouch diminished in size, the lips became thickened and the breast nipples turgid. One to two weeks after terminating the injections the pouch began to increase in size and within a further fortnight or less it reached its maximum size. This corresponded approximately to a pouch which could accommodate a large pouch young of about a tenth of the bodyweight of the mother. After the maximum extension had been reached slow involution extending over several months took place. These changes of the size and condition of the pouch were indicated by digital and visual examination as well as by the pouch capacity test. The following example (possum No. 101, bodyweight 2·4 kg.) will demonstrate this.

Experiment 101.

23/10/41. Gave birth to a young.

1/4/42. The large young of more than five months of age was taken away from the mother.

21/4/42. On examination the pouch was found to be still fairly large. It measured 5·0 cm. in depth (measurement was taken from the caudal end of the pouch-opening to the caudal end of the pouch (Bolliger and Carrodus, 1940*a*) and about 8 cm. in maximum width. On injecting water into the pouch (capacity test) 19 ml. were retained. The base of the right mammary gland to whose nipple the young was attached had a diameter of 1·2 cm. Left mammary gland and nipple were considerably smaller. 500 I.U. of gonadotropin obtained from human pregnancy urine were injected intramuscularly.

24/4/42. The pouch had already contracted in size. It was only 2·5 cm. in depth, the nipples were turgid and the mammary glands were smaller than they were before the injection. 500 I.U. gonadotropin were injected intramuscularly.

28/4/42. The pouch now measured only 1·5 cm. in depth. The nipples were very turgid and on pressure produced a white secretion. 500 I.U. of gonadotropin were administered.

30/4/42. The lips of the pouch were thickened and puckered. The depth of the pouch was 1·4 cm., and on injecting water only about 1 ml. or less was retained. The interior of the pouch was fairly dry and the white secretion previously observed had ceased. The nipples were still very turgid and the mammary glands were considerably smaller than they were before the injections were started.

4/5/42. By now the pouch had increased in size. It measured on an average 4·0 cm. in depth. The interior of the pouch was moist owing to the secretion of a light brownish fluid. The mammary glands had enlarged and the right mammary gland had reached approximately the pre-experimental size.

7/5/42. The pouch was found to be very large. It measured about 5·5 cm. in depth and 11 cm. in width. On injecting water into the pouch-cavity 46 ml. could be retained.

12/5/42. The pouch appeared to be still larger than on 7/5/42. In caudal direction it was found to reach down as far as the upper attachment of the medial thigh musculature and on injecting water 60 ml. could be retained. Mammary glands and nipples were comparatively small, measuring about similar dimensions as observed pre-experimentally.

13/5/42. The animal was killed. It was found to be in a very good state of nutrition and the urea content of the blood obtained just before the animal was killed was 32 mg. per cent.

On examining the genital tract, the ovaries were found to be enlarged and contained numerous large and small *corpora lutea* as well as some newly formed follicles. The uteri were markedly enlarged and contained large amounts of secretion. (Plate I.)

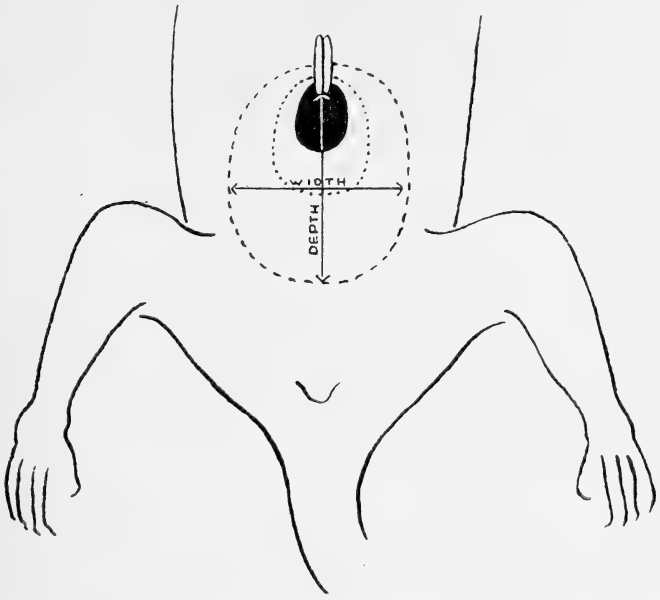


Fig. 1. Diagrammatic representation of the changes in the size of the pouch following the administration of gonadotropin obtained from human pregnancy urine. Dotted line represents pre-experimental size of the pouch. The black area represents the contracted pouch as observed shortly after the administration of the gonadotropin. Broken line indicates the enlarged pouch as observed about two weeks following the administration of gonadotropin.

In other experiments where the animal was not killed when the pouch had reached approximately maximum dimensions, this organ was found to remain at its maximum size for about a week or two. Then slow involution began to take place extending over two months or more and thus a large pouch of over 20 ml. in capacity brought on by injection of a total 1,500 I.U. may persist for three months.

Such a dosage as 1,500 I.U. does not interfere with the health of the animal. It is not yet certain if it will influence its fecundity. However, after the administration of a smaller dose of 800 I.U. the animal was found to give birth to young four months after terminating the injections.

Animals with persistently small, dry pouches which suggested temporary or permanent sterility due to known or unknown causes, also responded to the injections of gonadotropin though to a smaller extent. As with the former group of animals, the pouch, although already small, decreased after the administration of the hormone and then increased much in excess of its pre-experimental size. Again the capacity test demonstrated this very clearly as will be demonstrated in an animal which seemed to be in a state of sterility probably due to the administration of considerable amounts of the synthetic female sex hormone, stilbœstrol, which had been given for 15 months previously.

Experiment S3.

4/9/40.	1·5	mg.	of	stilbœstrol	administered	intramuscularly.
9/9/40.	1·5	,,	,,	,,	,,	,,
16/9/40.	1·5	,,	,,	,,	,,	,,

During the second half of 1941 the pouch remained about stationary in size and measured 3 cm. in depth and about 4·5 cm. in its maximum width. On injecting water into the pouch it was only capable of retaining 3 ml. (pouch capacity test). The interior of the pouch was dry and clean.

16/12/41. 250 I.U. of gonadotropin were injected intramuscularly.

19/12/41. 250 I.U. of Gonan were injected intramuscularly.

22/12/41. The depth of the pouch was now only 2 cm., and only 1 ml. of water was retained when executing the capacity test.

2/1/42. A day or two previously the pouch was found to increase in size and measured now 4·5 cm. in depth and about 6 cm. in maximum width. Its interior was moist, due to the presence of a light brown fluid. During the following week the pouch probably enlarged slightly further.

9/1/42. On executing the capacity test the pouch was found to retain 15 ml. of water. This enlarged pouch was found to persist for two more months. Then the animal was used for another experiment.

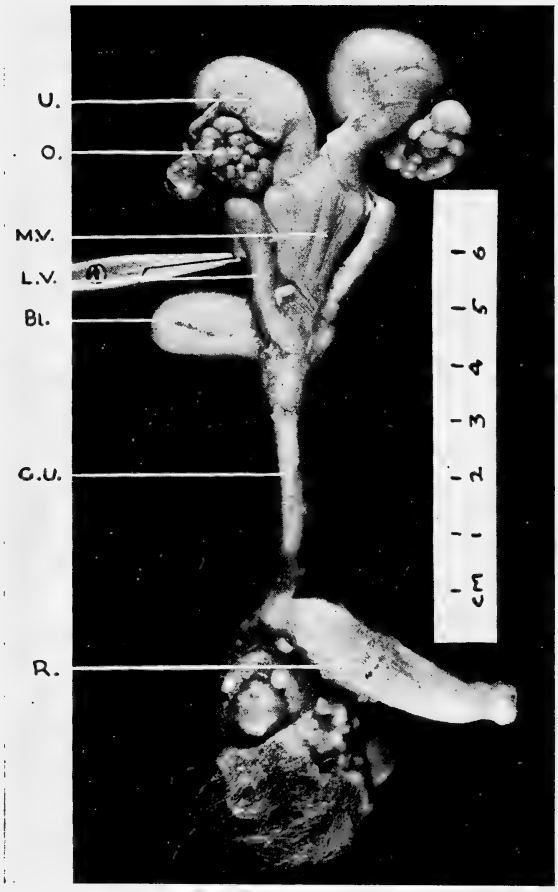
Discussion.

As pointed out before, spontaneous and considerable expansion of the pouch takes place immediately before the young of *Trichosurus vulpecula* is born. Following birth further expansion takes place to provide sufficient space for the rapidly growing pouch young. As shown in the experiments described in this paper, a similar enlargement can be brought on at any time by the administration of a fairly large dose of gonadotropin obtained from human pregnancy urine which, in the present study, was usually divided up into three injections. Since so far no other hormone has been found to give an equally marked reaction of this nature, it is assumed for the time being that a hormone similar or identical to that found in human pregnancy urine brings on the spontaneous enlargement of the pouch preceding birth and probably also the further enlargement during about three months afterwards, during which period the frail growing pouch young would have to be provided with the necessary space.

This widening effect as brought on by our gonadotropin is considered to be a typical reaction of the pouch, and not merely an extension of the mammary area, mainly because the increase in size of the mammary glands is only small when compared with the increase in size of the pouch, which as far as its capacity is concerned may be as much as twenty-fold. Furthermore, clearly, not only the lining of the pouch but also the areolar tissue surrounding it and situated between *panniculus carnosus* and abdominal musculature must play an important part in the extension and contraction of this organ. This, however, will be discussed on another occasion.

Furthermore, the cremaster muscle (*compressor mammæ*) must also be involved in this enlargement, because when the pouch increases in size under the action of the gonadotropin there is a movement of the mammary glands caudad. Consequently the cremasters have to extend in length while in the case of a contraction of the pouch there is a shortening of these muscles (Bolliger and Canny, 1941).

The process of enlargement of the pouch, after the administration of gonadotropin obtained from human pregnancy urine, is preceded by a definite contraction. As shown in previous experiments, contraction of the pouch is brought on by œstrogens (Bolliger and Carrodus, 1940*a*; Bolliger and Canny, 1941). Therefore some preliminary follicular stimulation and subsequent release of follicular hormone may be assumed to occur after the injection of gonadotropin from urine of pregnancy. This is supported by the histological appearance of the ovaries, which also show some newly formed follicles (Plate I).


U.
O.
M.V.
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G.U.
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However, it is a well recognised fact that the gonadotropin obtained from urine of pregnancy possesses mainly luteinising properties. This also seems to be the case in our marsupial judging from the appearance of ovaries and uteri after its administration. In male possums it also reacted as one would expect from a substance of this nature, i.e. in adolescent animals precocious development of the sex organs and spermatogenesis were produced after its administration (Bolliger, 1942). But as far as the pouch is concerned, the results obtained from our luteinising hormone do not agree with those obtained from the administration of the crystalline *corpus luteum* hormone, progesterone, which in higher mammals is produced by the *corpora lutea*, and which prepares the uterus for pregnancy. In our marsupial *Trichosurus vulpecula*, progesterone brought on a short-lived and not very marked enlargement of the pouch, together with an increase in the size of the mammary glands. This, then, was followed by a relaxation of the pouch, which lasted for some months. On the other hand, the gonadotropin used in the present experiments brought on a short-lived contraction followed by a marked expansion, but without definite loss of tone. This discrepancy cannot be explained at this stage.

Summary.

In the fully grown female diprotodont marsupial, *Trichosurus vulpecula*, gonadotropin obtained from human pregnancy urine brings on a preliminary contraction of the pouch, followed by a marked expansion which is somewhat similar to that seen just before a young is born. Within about two weeks following the initial contraction, the expansion of the pouch reaches about its maximum, which after the administration of about 1,500 I.U. of gonadotropin would allow the housing of a pouch young of about 1/10th of the body weight of the mother. This enlarged pouch persists for about a week then slow involution takes place, extending over one to three months.

This reaction indicates that the gonadotropin obtained from human pregnancy urine not only influences ovaries and uteri as in eutherian mammals, but also the pouch, an ectodermal structure, and that a similar hormone must play a vital part in marsupial reproduction which fully depends on a properly conditioned pouch.

References.

Bolliger, A., 1942. This Journal, **76**, 86.
Bolliger, A., and Canny, A. J., 1941. This Journal, **75**, 21.
Bolliger, A., and Carrodus, A., 1940*a*. This Journal, **73**, 218.
Bolliger, A., and Carrodus, A., 1940*b*. This Journal, **73**, 228.

Description of Plate I.

Plate I (Experiment 101). Genital tract of *Trichosurus vulpecula* (posterior aspect) treated with gonadotropin obtained from human pregnancy urine. Note enlarged uteri and ovaries. The ovaries are covered with numerous *corpora lutea* as well as some newly formed follicles.

U.=uterus ; O.=ovary ; M.V.=median vagina ; L.V.=lateral vagina ; Bl.=bladder ; G.U.=urogenital canal ; R.=rectum.

THE DEVONIAN RUGOSE CORALS OF THE TAMWORTH DISTRICT, N.S.W.

By Dorothy Hill, Ph.D., D.Sc.,
University of Queensland.

With Plates II-IV.

Manuscript received, July 15, 1942. Read, August 5, 1942.

Summary. In this paper four rugose reef-coral faunas are recognised and their species described; the Moore Ck. or *Sanidophyllum* fauna, the Sulcor or *Eridophyllum* fauna, the Loomberah or *Eddastræa* fauna and the Nemingha or *insigne* fauna. The first is deduced to be Givetian and has affinities with the Queensland Burdekin fauna; the second is thought to be early Couvinian and has species in common with the Loyola fauna of Victoria and with the Murrumbidgee fauna of New South Wales; the third is possibly early Couvinian, and the last either late Lower Devonian or very early Couvinian, with affinities to the Silverwood fauna of Queensland.

Most of the material studied consisted of thin sections cut in the University of Sydney by Mr. H. G. Gooch, from specimens collected by Dr. Ida Brown, while the remainder consisted of sections and specimens in the Australian Museum and the University of Queensland. Dr. Brown's interpretation of the stratigraphy of the Attunga area to the north of Tamworth is shown on her map, published on page 168 of this volume. Her work, following on that of Benson, indicates that limestones are developed on three horizons in the area, the lowest forming the Nemingha group, the middle the Loomberah-Sulcor group, and the upper the Moore Ck. The results obtained from a study of the rugose corals are in general agreement with this.

The lists of Rugose corals obtained from the various localities and determined by thin sections are as follows:

Moore Ck. Limestone (R. 1472, pors. 111, 61 and 136, Par. Woolomol): *"Cystiphyllum" australe, Mesophyllum cornubovis, Disphyllum robustum, Phacellophyllum porteri, Sanidophyllum colligatum, S. davidis, Spongophyllum giganteum, S. ? immersum, S. halysitoides.*

Springs Ck. Limestone (Tamworth Common, 1 mile north of Tamworth): *Dohmophyllum* sp., *Xystriphyllum mitchelli, "Campophyllum"* cf. *lindstromi, Disphyllum robustum, Phacellophyllum porteri, Sanidophyllum davidis.*

Woolomol Limestone (Pors. 41, 42, Par. Woolomol): *"Cystiphyllum" australe, "Campophyllum"* cf. *lindstromi.*

Limestone in southern end of Por. 137, Par. Woolomol: *Spongophyllum ? immersum, Sanidophyllum* sp. (from hand specimen only).

Follington's Limestone in north part of Por. 252, Par. Burdekin: *Phacellophyllum porteri* (7179), *Sanidophyllum* sp. (from hand specimen only), *? Tryplasma* sp., *Spongophyllum giganteum.*

Limestone in N.E. part of Por. 248, Par. Burdekin: *Disphyllum* cf. *gregorii, Spongophyllum giganteum.*

Limestone in Por. 127, Par. Burdekin: *Sanidophyllum colligatum, Stringophyllum bipartitum, S. densum.*

Limestone in Por. 264, Par. Burdekin : *Sanidophyllum* sp., *Favistella* cf. *rhenana* ; in S.W. corner, *Sanidophyllum davidis* ; in central-eastern part, *Sanidophyllum colligatum.*

Limestone in Por. 249, Par. Burdekin, central-eastern part : *Disphyllum* cf. *Phacellophyllum porteri, Sanidophyllum colligatum.*

Sulcor Limestone (Pors. 88 or 115, Par. Burdekin) : *Xystriphyllum magnum, Prismatophyllum brownæ, Trapezophyllum coulteri, Phillipsastræa maculosa, P. linearis, P. carinata, Eridophyllum bartrumi, Mictophyllum* cf. *cresswelli, Aulacophyllum trizonatum, Pseudamplexus princeps.*

Limestone in the S.W. corner of Por. 248, Par. Burdekin : *Xystriphyllum mitchelli.*

Limestone in the N.E. corner of Por. 193, Par. Burdekin : *Prismatophyllum brownæ.*

Loomberah Limestone (Por. 23, Par. Loomberah, west bank of Sandy Ck.) : *Eddastræa grandis, Phillipsastræa aperta, P. cuncta, Endophyllum* cf. *abditum.*

Nemingha Limestone (Beedle's Freehold, Por. 163, Par. Nemingha) : *Pseudamplexus* sp., *Spongophyllum halysitoides.*

Limestone in Por. 181, Par. Nemingha : *Favistella neminghensis.*

Limestone in Por. 256, Par. Burdekin : *Acanthophyllum* cf. *mansfieldense, Lyrielasma floriforme, Xystriphyllum insigne.*

Limestone in Por. 277, Par. Burdekin (middle of south boundary near Por. 184, and N.W. corner) : *Lyrielasma floriforme.*

Limestone in Por. 15, Par. Burdekin : " *Cystiphyllum* " *multitrabeculatum.*

Limestone in Por. 192, Par. Attunga, W. side of Boundary Ck., north of Moore Ck. : *Tryplasma* sp. (slender, fasciculate).

A study of the lists shows that there are four localities with enough species present for faunal discussions ; these are Moore Ck., Sulcor Qy., Loomberah, and Por. 256, Par. Burdekin. None of these localities contains species found in any of the other three. The lists also show that the coral faunas in each case are coral-reef faunas, so that any differences in associations must be due to age or location, and not to facies.

The Moore Ck. list is mostly from old collections, from specimens labelled merely " Moore Ck." The map in Carne and Jones (1919, opp. p. 254) shows seven separate limestone patches in this " Moore Ck." locality, and it may be that more than one horizon is represented. Thus the record of *S. halysitoides*, known elsewhere from the type locality for the Nemingha limestone, may mean that one of the limestone patches is the equivalent of the Nemingha. Dr. Brown considers that a Nemingha equivalent occurs on the north side of Moore Creek. By identity of species contained, it is reasonable to correlate the following limestones with the Moore Ck. : Springs Ck. ; Woolomol ; Follington's ; N.E. part of Por. 248 (probably 232), Par. Burdekin ; 137 Par. Woolomol ; Por. 127, Par. Burdekin ; Por. 264, Par. Burdekin ; and central-eastern part of Por. 249/232, Par. Burdekin. With the Sulcor limestone we may correlate the limestone in the N.E. corner of Por. 193, Par. Burdekin, as both contain *P. brownæ*. The Loomberah limestone shows no identity of species with any other. With the limestone in Por. 256, Par. Burdekin, we may correlate that in the middle of the south boundary of Por. 277, Par. Burdekin, near Por. 184, in Por. 192, Par. Attunga, and in the N.W. corner of Por. 277, and tentatively the " Nemingha " limestones of Benson from Beedle's Freehold (Por. 163, Par. Nemingha) and Por. 181, Par. Nemingha, although there is no identity of species between Benson's localities and Brown's new ones ; the correlation is made on the lithological characters of the breccia, etc., noted by Brown above the limestones in each case.

The ages suggested by comparing the four faunas with those of the standard foreign successions and of other localities in Australia are as follows :

Moore Ck.-Springs Ck. (Sanidophyllum) Fauna.—Givetian. *Dohmophyllum* suggests the Lower or Middle Givetian ; *Xystriphyllum mitchelli* suggests the Couvinian ; "*Cystiphyllum*" *australe* indicates broadly the Middle Devonian ; *Mesophyllum cornubovis* suggests the lower Givetian, *Disphyllum robustum* the Couvinian, and *Phacellophyllum porteri* the Givetian or Frasnian. *Sanidophyllum* is unknown elsewhere. *Spongophyllum giganteum* resembles *S. varians* from the Middle Devonian of the Eifel. *S. immersum* is known from the Middle Givetian in Queensland. *S. halysitoides* is typical of the Nemingha limestone while a variety occurs in the Couvinian Silverwood limestone. On the whole the Moore Ck.-Springs Ck. fauna appears to have Givetian affinities, and this deduction is strengthened by the occurrence of *Stringophyllum bipartitum* and of specimens comparable with *Disphyllum gregorii* and *Favistella rhenana*, all three of which occur in the middle Givetian of Queensland, in outcrops which may be correlated with the Moore Ck. limestone.

Sulcor (Eridophyllum) Fauna.—Early Couvinian (early Murrumbidgee). The only species which is closely comparable with foreign species is *Eridophyllum bartrumi*, which occurs in the lower Middle Devonian of Reefton, N.Z., while a closely similar species is known from the lower part (? Couvinian) of the Middle Devonian Nevada Limestone of the U.S.A. *Xystriphyllum* occurs in the Lower Devonian of the U.S.A. and Bohemia ; *Prismatophyllum*, *Phillipsastræa* and *Mictophyllum* are known from the Lower, Middle and Upper Devonian elsewhere, and *Pseudamplexus* in the Silurian, Lower and Middle Devonian ; *Aulacophyllum* occurs in the Middle Devonian Columbus and Hamilton limestones of the U.S.A. These comparisons suggest a lower Middle Devonian age, but comparison with Australian faunas whose ages have been separately deduced gives serviceable results also. *Xystriphyllum magnum* occurs in the Murrumbidgee fauna as developed in the Wellington district of N.S.W., and thus indicates the Couvinian ; *Prismatophyllum brownæ* is unknown elsewhere. *Trapezophyllum* is known elsewhere only from the ? Lower Devonian Loyola limestone of Victoria. *Phillipsastræa maculosa* and *P. linearis* occur also in the Loyola limestone, and *P. carinata* in the Coblenzian Mt. Etna limestone. *Eridophyllum bartrumi* is characteristic of the Couvinian Murrumbidgee fauna ; *Mictophyllum cresswelli* is known from the Lower or Middle Devonian Lilydale limestone of Victoria. *Aulacophyllum trizonatum* is not known elsewhere. *Pseudamplexus princeps* occurs in Lower and lower Middle Devonian limestones in N.S.W. and Queensland. The assemblage thus suggests a horizon intermediate between the Garra (Mt. Etna) Coblenzian and the Murrumbidgee Couvinian, possibly low in the Couvinian. The two species common to the Sulcor and the Loyola limestones suggest that they are of approximately the same age, and the Loyola limestone may well be very low in the Couvinian rather than Lower Devonian as previously suggested ; or, it may be, that the Sulcor Limestone is very high in the Lower Devonian, but the former seems to me more likely. It should be stated, however, that our knowledge of the coral faunas existing in the European type areas at the top of the Lower Devonian and the beginning of the Middle Devonian is still too incomplete to form a really reliable guide as to which side of the boundary any one fauna found in Australia should be placed.

The Loomberah (Eddastræa) Fauna.—Possibly Couvinian, early. *Eddastræa* occurs in the Lower Devonian of Ellesmereland ; *Phillipsastræa* is Lower, Middle and Upper Devonian in range, and *Endophyllum abditum* is a Middle Devonian species in Europe and Asia. The age vaguely indicated by these oversea comparisons is thus perhaps early Middle Devonian. *E. grandis* occurs in the Telamon limestone of Queensland, in association with *Xystriphyllum*

insigne and *Acanthophyllum* cf. *mansfieldense*, two species which suggest correlation with the Nemingha fauna. *Phillipsastræa aperta* occurs in the Wellington district at an unknown horizon, in association with a different species of *Eddastræa*. *P. callosa* is unknown elsewhere. The affinities of this small Loomberah fauna are by no means clear, but a horizon near the boundary between Coblenzian and Couvinian is suggested, possibly on the Couvinian side.

The Nemingha (insigne) Fauna.—Lower Devonian or possibly early Couvinian. The fauna of the type Nemingha limestone is very scant. It contains only *Pseudamplexus* sp. and *Spongophyllum halysitoides*, both of which are known in the Silverwood limestones, previously deduced to be Lower Couvinian. If we accept the lithological correlations made by Dr. I. Brown, and these indeed seem reasonable, we may argue from a larger fauna, by adding *Acanthophyllum* cf. *mansfieldense*, *Lyrielasma floriforme* and *Xystriphyllum insigne* from the limestone in portion 256-277, Par. Burdekin, and *Tryplasma* sp. from that in Por. 192, Par. Attunga. The first suggests the upper part of the Lower Devonian or low in the Couvinian, *Lyrielasma* is known in the Lower and Middle Devonian while *X. insigne* is characteristic of the early Couvinian Silverwood limestone, and of the Chillagoe limestone, at present regarded as Silurian. *Tryplasma* suggests a pre-Middle Devonian correlation. Either a Lower Devonian or an early Couvinian age is thus possible.

The Rugose corals thus indicate that the Nemingha group of limestones is the oldest, either late Lower Devonian or very early Couvinian, and the Moore Ck. the youngest, being Givetian. The Sulcor and Loomberah limestones, though containing no species in common, both appear to be early Couvinian, but we are unable to deduce their relative stratigraphical position from their faunas. We also have the interesting result that the Loyola fauna of Victoria is not far in stratigraphical position from the Sulcor limestone.

It is remarkable that no one species is common to any two of the four faunas. But the Loomberah is connected with the Nemingha by both the Telamon and the Silverwood faunas, of Queensland. The Sulcor has close relations with the Loyola of Victoria, but is also related to the Murrumbidgee, while it has two species in common with the Garra (=Mt. Etna) fauna, which is thought to be older than the Silverwood and Nemingha faunas. The Moore Ck. is divorced entirely from all seven of these other faunas, but is related to the Givetian Burdekin fauna of Queensland. The very sharp division here may indicate a disconformity or a migration.

Systematic Descriptions.

Family **Acanthophyllidæ** Hill, 1939*b*, p. 220; 1942, p. 234.

The cerioid genus *Xystriphyllum* Hill, 1939*a*, p. 62, previously placed somewhat doubtfully in the Spongophyllidæ, is herein removed to the Acanthophyllidæ. It was referred to the Spongophyllidæ because the genotype, *X. dunstani* (Etheridge), showed occasional lonsdaleoid dissepiments, and was associated with a cerioid species of *Spongophyllum*, which is morphologically closely similar and from which it was thought to have been derived. But in view of the large number of species of *Xystriphyllum* now known, which have acanthophylloid rather than spongophylloid septal and tabular arrangements, and the fact that lonsdaleoid dissepiments are rather rare in the genus, it is considered that the morphological resemblance to the Spongophyllidæ is homeomorphic rather than phylogenetic; although the other possibility, that *Spongophyllum spongophylloides* (Etheridge) may have been derived from *Xystriphyllum* rather than from *Grypophyllum*, like the genotype of *Spongophyllum*, is very strong.

Genus **Acanthophyllum** Dybowski ; Hill, 1939*b*, p. 222.

Acanthophyllum ?mansfieldense (Dun). (Pl. II, fig. 1.)

One specimen, U.S. 7254, from the Nemingha limestone of Por. 256, Par. Burdekin, is close to *A. mansfieldense* (Dun ; Hill, 1939*b*, p. 223) from the ? Lower Devonian limestone of Loyola in Victoria. It is slightly smaller in diameter, and has fewer septa, 21 of each order as against 26 ; also, it has a greater degree of septal dilatation, the loculi between the septa being almost completely filled. Acanthophyllids with great septal dilatation occur also in the Silverwood, Telamon, Garra and Mt. Etna limestones.

Genus **Dohmophyllum** Wedekind ; Hill, 1942, p. 236.

Dohmophyllum sp. (Pl. IV, fig. 1.)

Material. One specimen, F 6199, Australian Museum 179, from the Moore Ck. limestone in Springs Ck. near Tamworth.

Diagnosis. Dohmophyllum with 35 septa of each order, some being thickened or buttressed by lateral dissepiments.

Description. The thin section, which is somewhat oblique, has a shorter diameter of 45 mm. and a longer of 60 mm. There are 35 septa of each order, the major extending to the axis, where they interdigitate in the manner characteristic of the Acanthophyllidæ, and some are rotated ; they are a little dilated in the tabularium, which is very narrow, only 10 mm. at most in diameter. The minor septa are almost as long as the major, but are thinner ; the septa of both orders may be dilated or buttressed by lateral dissepiments. The dissepiments are small and equal, and the dissepimentarial floors are flat or even somewhat everted in the broad peripheral regions, but slope steeply downwards into the tabularium ; the tabular floors are formed of close, flattened tabellæ, without a median notch, and are irregular, domed and sagging in different parts of the same floor.

Remarks. As only one specimen is available, a complete understanding of the species is not possible. It has not the axial structure of discrete septal ends found in the more typical *Dohmophyllum*, and it shows septal modifications, in the presence of lateral dissepiments, not found in the north Queensland Givetian *D. clarkei.*

Genus **Lyrielasma** Hill, 1939*b*, p. 243.

Lyrielasma floriforme sp. nov. (Pl. II, fig. 2.)

Holotype. S.U. 7252, limestone in middle of south boundary, Por. 277, Par. Burdekin. Probably an equivalent to the Nemingha Limestone.

Diagnosis. Lyrielasma with a narrow, nearly regular peripheral stereozone.

Description. The corallum is compound and fasciculate, the corallites being unequal, from 2 to 17 mm. in diameter (average of 10 mm.), and unequally spaced. The nature of the increase is unknown. There are typically 20 septa of each order, the major extending unequally to the axis, and the minor about two-thirds as long. They are all dilated at the periphery to form a peripheral stereozone 1 mm. wide, the dilatation then decreasing suddenly towards the axis, but recurring irregularly in the middle course of the septa. The tabularium is about 3 mm. wide in the average corallite, and the tabular floors are concave with a median notch, the tabulæ being complete or incomplete, and very close. The dissepiments are small and rather globose, gently inclined near the periphery and steeply inclined near the tabularium.

Localities. Type, as above ; north-west corner of Por. 277, Par. Burdekin, and S.U. 8151, Por. 256, Par. Burdekin. All are considered to be on the horizon

of the Nemingha limestone by Dr. I. A. Brown, by reason of the similarity of lithology.

Remarks. The species is considered to belong to *Lyrielasma* rather than to *Grypophyllum*, which is morphologically somewhat similar but is regarded as a member of the Spongophyllidæ, because it shows the septal dilatation of the former, and is without the degeneration of the minor septa so characteristic of the latter.

Genus **Xystriphyllum** Hill, 1939*a*, p. 62 ; 1940*c*, p. 269.

See remarks under Family Acanthophyllidæ.

Xystriphyllum magnum sp. nov. (Pl. III, figs. 2*a*, 2*b*.)

Holotype. S.U. 7270, behind the Sulcor Quarry, in Pors. 88 and 115, Parish of Burdekin, near Attunga.

Diagnosis. *Xystriphyllum* with large corallites, up to 20 mm. in diameter, and about 22 long septa of each order.

Description. The corallum is cerioid and large. The corallites are up to 20 mm. in diameter, and are five or six-sided, the sides being usually straight, but sometimes curved. There are 22 septa of each order in the larger corallites ; they are long, and typically without curvature, even in the tabularium, where the ends of the major septa may interdigitate to some depth ; they may be slightly wavy, and occasionally are discontinuous near the periphery, when lonsdaleoid dissepiments may occur ; the minor septa extend nearly three-quarters of the way to the axis. There is no septal dilatation, and the minor septa are somewhat thinner than the major. The tabular floors are close, shallowly concave with a median notch, and are formed by elongate tabellæ. The tabularium has a diameter only about one-quarter that of the corallite. The dissepiments are rather large, flat lying near the periphery, but globose in intermediate areas and steeply inclined near the tabularium ; some are geniculate in transverse section, and others buttress the sides of the septa.

Localities. In addition to the type locality, the species occurs north of the road, Por. 247, Parish of Micketymulga, about 6 miles N.W. of Wellington. Its horizon is thought to be early Murrumbidgee, i.e. early Couvinian.

Xystriphyllum mitchelli (Etheridge). (Pl. II, fig. 9.)

Hill, 1940*c*, p. 269, pl. XI, figs. 2, 3, Murrumbidgee (Couvinian) beds.

New Localities. Springs Ck. (Australian Museum F 4204) ; and south-west corner of Por. 248, Par. Burdekin (S.U. 7251) ; both in the Tamworth district.

Xystriphyllum insigne Hill.

Hill, 1940*a*, p. 164, pl. III, figs. 5*a*, *b*, Lower Middle Devonian of Limestone Siding, Silverwood, Q.

Localities. Limestone in Por. 256, Par. Burdekin (=limestone on the Manilla road, 15 miles from Tamworth, near Attunga, and limestone 2 miles N.W. of Attunga), mapped by Dr. I. A. Brown as an equivalent of the Nemingha limestone.

Genus **Eddastræa** nov.

Genotype. *Phillipsastræa grandis* Dun in Benson, 1918, p. 379, pl. XXXV, figs. 4, 5, Loomberah limestone.

Diagnosis. Astræoid, thamnastræoid or aphroid Rugose corals with wide dissepimentaria of small, highly arched dissepiments, with shallowly concave,

axially deepened tabulæ, and with long, but unequal major septa. The axial ends of the major septa are arranged in groups in the tabularium, and are straight or curved vortically, the curvature differing in degree from group to group; the cardinal septum is typically short.

The genus contains the plocoid members of the Acanthophyllidæ, just as *Lyrielasma* includes the phaceloid and *Xystriphyllum* the cerioid members. It is quite unrelated morphologically to the co-existent and also plocoid *Phillipsastræa*, differing from this member of the Disphyllidæ in just those characters in which *Macgeea*, the solitary Disphyllid, differs from Acanthophyllum, the solitary Acanthophyllid. The genus occurs elsewhere in the Lower Devonian of Ellesmereland, in *Phillipsastræa gigas* of Loewe (1914, pl. IV, fig. 2).

Eddastræa grandis (Dun).

Phillipsastræa grandis Dun in Benson, 1918, p. 379, pl. XXXV, figs. 4, 5, Loomberah limestone.

? Spongophyllum (?) sp. n. Dun in Benson, *id.*, pl. XXXIV, figs. 2, 3.

Diagnosis. *Eddastræa* with large corallites.

Type Material. The specimen figured by Dun has not been traced.

Description. The corallum is plocoid, the common wall between corallites being absent, and in Dun's figured specimen (figs. 4, 5) the septa of neighbouring corallites are confluent. The corallites in this figured specimen are about 20 mm. apart from axis to axis, varying between 16 and 25 mm. The tabularia are narrow, only 4 mm. wide, while the dissepimentaria are exceptionally wide. There are 20 to 23 septa of each order, the major extending unequally to the axis in groups, the groups being curved aside to greater or less degrees. They may show carinæ in the tabularium. The minor septa are a little thinner than the major, and a little shorter. The dissepiments, which are small, are almost horizontally inclined at the junctions of the corallites, but towards the axis they become steeper and where they line the tabularium they are vertical. The tabulæ are small, elongate, close and thin, forming concave tabular floors with a median deepening.

Remarks. The similarity in internal structure of corallites between this plocoid species and the cerioid *Xystriphyllum magnum* of the Sulcor limestone is very great. Possibly the specimen figured by Dun as *Spongophyllum loc. cit.* is a member of the species *E. grandis*, but the septa of neighbouring corallites abut against one another rather than run together, the corallites are smaller and there are fewer septa, with a maximum of only 17 of each order as against 23. The characters of the septa, dissepiments and tabulæ are otherwise very similar. The species is very like the Lower Devonian *Phillipsastræa* of Loewe from Ellesmereland. It has also been collected from the limestone near Telamon, on the Springsure-Tambo road, Queensland.

Family **Caniniidæ**; Hill, 1939*c*, p. 102.

Genus "**Campophyllum**" Auctt.; Hill, 1940*c*, p. 254.

"**Campophyllum**" cf. **lindstromi** (Frech). (Pl. IV, figs. 2*a*, 2*b*.)

Two specimens, F 6201, Australian Museum, from the Moore Ck. limestone of Springs Ck., and S.U. 7152 from the Woolomol limestone of Pors. 41, 42, Par. Woolomol, have the general morphology of "*C.*" *lindstromi* (Frech, 1885, p. 38; 1886, p. 69, pl. I, figs. 8-12, 14-17) from the Givetian and Upper Devonian of Germany, which appears not to have been re-studied or subdivided. The Springs Ck. specimen is a cylindrical fragment about 30 mm. in diameter,

somewhat compressed, with 44 major and 44 minor septa, the major extending about half-way to the axis and the minor being only about 5 mm. long. They are all rather thin throughout, and the major septa are somewhat irregular in course in the tabularium. The tabularium is wide, about 22 mm. in diameter, with horizontal and usually complete tabulæ, which sometimes, however, do not extend quite across the tabularium, but have one margin on the plate below. The dissepiments are small but unequal, seldom geniculate. The age indicated is Givetian or Upper Devonian.

Cystimorphs ; Hill, 1939*b*, p. 248 ; 1942, p. 241.

"**Cystiphyllum**" **australe** Etheridge ; Hill, 1942, p. 243.

Typical specimens are U.Q. 20012 from the Moore Ck. limestone of Moore Ck. and S.U. 6249 from the Woolomol limestone of Pors. 41, 42, Par. Woolomol. In Queensland the species is characteristic of the Givetian limestones ; but specimens thought to form a related group occur in the Couvinian Murrumbidgee limestones of N.S.W.

"**Cystiphyllum**" **multitrabeculatum** sp. nov. (Pl. II, figs. 3*a*, 3*b*.)

Holotype. S.U. 7214, limestone in Por. 15, Par. Burdekin, mapped by Dr. I. Brown as equivalent to the Nemingha limestone.

Diagnosis. Cystimorph in which the arrangement of the very numerous trabeculæ into septa is still apparent.

Description. The corallum is probably solitary, and the diameter more than 50 mm. There are more than 80 septa in all in the transverse section provided, but it has not been possible to distinguish the minor septa with certainty from the major, although presumably the minor extend to the inner edge of the dissepimentarium, which is not clearly separable from the very narrow tabularium. Each septum consists of two series of holacanthine trabeculæ, diverging pinnately from the median plane, and set in a continuous mass of lamellar sclerenchyme. In most parts of the transverse section, some of the dissepiments cause discontinuities in the septa, but in places the septa are continuous from periphery to tabularium. One septum may be traced right beyond the axis of the corallum, and this would appear to be in the counter fossula ; but it could not be determined whether it was the very long counter minor septum so characteristic of the Digonophyllidæ. It is, like the latter, in the plane of symmetry of the corallum. The septa are curved towards the cardinal septum, which is short. The tabularium is eccentric, and is nearer to the cardinal margin than the counter, though still in the plane of symmetry of the corallum. The dissepiments are numerous and large, without exaggerated globosity, and fairly steeply sloping, not clearly distinguishable from the tabulæ, although these are a little larger and more horizontally inclined. The sclerenchyme seen in vertical section on the upper surfaces of the dissepiments and tabulæ is shown by the transverse section to be septal in origin.

Remarks. The specimen is most interesting, its septal morphology suggesting that it is a link between the Digonophyllidæ and those cystimorphs of the Middle Devonian which have for septal apparatus only holacanthine trabeculæ set in lamellar sclerenchyme ; but many more specimens must be found before such an important conclusion could be proved. None of the specimens figured by Wedekind and Vollbrecht (1931) from the Middle Devonian of the Eifel shows this arrangement of the trabeculæ in radial series corresponding to septa. As its morphology is so unusual, the specimen cannot be used as an indicator of age.

Family **Digonophyllidæ**; Hill, 1942, p. 244.

Genus **Mesophyllum** Schluter; Hill, 1942, p. 245.

Mesophyllum cornubovis (Etheridge). (Pl. IV, figs. 3, 4.)

Actinocystis ? cornubovis Etheridge, 1899, p. 159, pl. XXI, figs. 1, 2, pl. XXXVIII, fig. 1, Moore Ck. and Woolomol limestones, Tamworth.

Type Material. Not located, probably in the collection of the Geological Survey of New South Wales.

Diagnosis. *Mesophyllum* with the septa completely withdrawn from the periphery and typically from the axis also, and with minor septa suppressed, leaving a somewhat irregularly developed collar of long major septal segments in the inner parts of the dissepimentarium.

Description. The corallum is large and awl-shaped, with a long cylindrical or somewhat compressed distal portion. There are about 50 major septa, which are developed only as short septal crests on the dissepiments in the peripheral parts, but form long segments continuous through several series of dissepiments in the inner parts of the dissepimentarium; in one or two corallites they continue into the tabularium as continuous plates, and are a little dilated there. There are a few discrete cross-bar trabeculæ developed in the peripheral parts where the septa are suppressed. Minor septa are usually not developed at all, but in places they are represented by short crests on the dissepiments. The dissepiments are large and globose, often nearly circular in transverse section of the corallum in the outer parts where they can develop free of interference from the septa. In the interseptal loculi they are somewhat irregular, sometimes geniculate or inosculating. The tabularium is narrow, only about 10 mm. wide, and the tabular floors are horizontal or sagging, formed either of complete tabulæ or of globose tabellæ somewhat larger than the dissepiments. The dissepiments in vertical section are horizontally based near the periphery, but towards the axis become more and more inclined until at the tabularium they are vertical.

Remarks. There are many solitary coralla in the limestones around Tamworth which belong to the genus *Mesophyllum*, but I have thin sections from four coralla only. The sections appear to provide evidence that the species is very variable, one showing the major septa projecting into the tabularium and only a little withdrawn from the periphery, another with them developed as a collar in the inner half of the dissepimentarium, a third with only short segments developed only in this inner half, and the fourth with practically no septal segments at all. In none are the minor septa developed. But with so few sections, the evidence is incomplete, and the species cannot be accorded its full potential value for detailed stratigraphical correlation. The structure described above as typical is very like that of *Hemicosmophyllum corticosum* Wedekind and Vollbrecht from the Gerolstein railway cutting, in the Eifel, in the lower part of the *Stringocephalus* (Givetian) beds, and of the sub-genus *Atelophyllum* Wedekind from the upper Honsel beds of Emst, near the top of the lower part of the *Stringocephalus* beds. The species is distinguished from the north Queensland Givetian *M. collare* Hill (1942, p. 246) by the absence of minor septa.

Family **Disphyllidæ**; Hill, 1939*b*, p. 224.

Genus **Disphyllum** de Fromentel; Lang and Smith, 1935, p. 544.

Disphyllum robustum (Etheridge). (Pl. IV, figs. 5, 6.)

Diphyphyllum robustum Etheridge, 1899, p. 153, pl. XXXII, figs. 1, 2, pl. XXXVII, fig. 2; Moore Ck. limestone, Moore Ck., near Tamworth.

Holotype. M 571, Eth. Australian Museum Collection, Moore Ck., figd. Etheridge, pl. XXXII, fig. 1.

Diagnosis. Phaceloid Rugosa with three or four irregular series of dissepiments, minor septa but little shorter than major, and wide, close, complete, very slightly concave tabulæ.

Description. The corallum is phaceloid, and the corallites are long, straight and cylindrical, about 9 mm. in average diameter. There are typically 21 or 22 septa of each order, the major extending about half-way to the axis, and the minor being almost as long. The septa are thin and broadly wavy. The dissepiments are unequal in size and inclination, arranged in three or four irregular vertical series, none of them of horse-shoe type. The tabularium, which is typically about 5 mm. wide, contains very closely spaced, usually complete and slightly sagging tabulæ.

Remarks. The morphology of this species is close to that of the American Couvinian group of species placed in *Cylindrophyllum* Simpson (which Lang and Smith have regarded as a synonym of *Disphyllum*), though the inequality of dissepiments distinguishes our species from the American. *D. robustum* is easily distinguished from *P. porteri* by the absence of horse-shoe dissepiments.

Localities. Moore Ck., Springs Ck.

Disphyllum cf. **gregorii** (Etheridge). (Pl. IV, fig. 9.)

A single transverse section, S.U. 7263, sent to me from the limestone in the N.E. part of Por. 248, Par. Burdekin, differs from the typical specimens from Queensland (Hill, 1942, p. 247) only in having fewer septa—19 of each order as against 30. In Queensland the species is characteristic of the middle Givetian Burdekin series.

Genomorph **Phacellophyllum** Gurich ; Lang and Smith, 1935, p. 546.

Phacellophyllum porteri (Etheridge). (Pl. IV, figs. 7, 8.)

Diphyphyllum ? porteri Etheridge, 1890, p. 19, pl. I, figs. 7-11, Tamworth.

Type Material. Not traced. The species is interpreted on specimens named *D. porteri* by Etheridge in the Australian Museum collection, which agree in all respects with his description. These are F 6199 from Springs Ck. and F 6149 from Moore Ck.

Diagnosis. Phacellophyllum with the inner series of horse-shoe dissepiments and the outer series of flat dissepiments, and with complete, flat, distant tabulæ.

Description. The corallum is phaceloid, and the corallites are long, slender and cylindrical, usually with the outer series of flat dissepiments weathered off, when the diameter is 3 or 4 mm. ; when the outer series of dissepiments is preserved, the diameter may be 5 mm. There are 19 or 20 septa of each order at a diameter of 5 mm. ; these are usually minutely waved, and are somewhat dilated in the zone of the horse-shoe dissepiments, the dilatation extending over the surfaces of these dissepiments. The major septa extend half-way or less to the axis, and the minor septa go no further than the inner surfaces of the horse-shoe dissepiments. The horse-shoe dissepiments are very small, being less than 0·5 mm. wide, and are arranged fairly regularly one above the other in a single vertical series ; the outer flat dissepiments are also very small, similar in width to the horse-shoe plates. Usually this outer series is weathered off and the septa project from the corallite like the cogs from a cog-wheel. The tabulæ are complete, flat and distant.

Localities. Springs Ck. ; Tamworth Common, 1 mile north of Tamworth ; Moore Ck. ; Follington's limestone in north part of Por. 252, Par. Burdekin.

Remarks. The species indicates broadly a Givetian or Frasnian age. It differs from the European Givetian and Frasnian *P. trigemme* in not having an

outer series of tabellæ declining to the tabulæ, and from the Frasnian *P. minus* in having an outer series of dissepiments.

Genus **Prismatophyllum** Simpson ; Hill, 1939*b*, p. 229.

Prismatophyllum brownæ sp. nov. (Pl. III, figs. 4*a*, 4*b*.)

Holotype. S.U. 8152, limestone near Sulcor Quarry, Pors. 88 and 115, Par. Burdekin, near Attunga, N.S.W. ? Lower Couvinian.

Diagnosis. Prismatophyllum with a regular cylinder of horse-shoe dissepiments girdling the tabularium, and numerous outer dissepiments typically declined from the cylinder to the periphery.

Description. The corallum is cerioid, and the corallites are sub-equal and usually six-sided, of average diameter about 6 or 7 mm. There are 15 or 17 septa of each order, the major nearly reaching the axis, usually leaving a very small axial space ; the minor septa extend a little over half-way to the axis. Both orders are somewhat dilated at the position of the cylinder of horse-shoe dissepiments. The dissepiments are small, and the series next to the tabularium is of horse-shoe shaped plates arranged in a regular cylinder ; the outer dissepiments are always in more than one series and typically they are declined from the cylinder to the periphery. There may be considerable extension of the dilatation of the septa over the surfaces of the horse-shoe dissepiments. The tabular floors are low, flat-topped domes, about 2 to a mm., the flat part being that in the axial space free from septa ; they are of complete tabulæ, or of rather large flat tabellæ.

Remarks. This is the only species of *Prismatophyllum* known to me with horse-shoe dissepiments regularly developed into a cylinder. It differs from typical *Trapezophyllum* in that the outer dissepiments are not modified into flat plates. The age indicated is Devonian. S.U. 7236 from the N.E. part of Por. 193, Par. Burdekin, has larger corallites, up to 10 mm. average diameter, and more septa (21 of each order), while in parts of some corallites the outer dissepiments are declined from the periphery to the cylinder. This represents a considerable variation from the typical, but I have too few specimens from Sulcor Quarry to give a full account of the variation possible at the type locality, and for the present the specimen from Por. 193 is included in *P. brownæ*.

Genus **Trapezophyllum** Etheridge ; Hill, 1939*b*, p. 234.

Trapezophyllum coulteri sp. nov. (Pl. III, figs. 3*a*, 3*b*.)

Holotype. S.U. 5243, Sulcor Quarry, in Por. 88, Par. Burdekin, near Attunga. ? Lower Couvinian.

Diagnosis. Trapezophyllum with major septa extending almost to the axis, and with septa thickened in the region of the horse-shoe dissepiments.

Description. The corallum is cerioid, with unequal, four to six-sided corallites of average adult diameter about 6 mm. ; increase is peripheral, modifications occurring in the outer dissepimentarium of larger corallites in small areas which quickly become epithecate hystero-corallites. There are on the average 14 major and 14 minor septa ; the major extend almost to the axis, leaving a more or less regular axial space ; the minor are a little over half as long ; both orders are dilated in the region of the horse-shoe dissepiments, and the dilatation extends over the surface of the horse-shoe dissepiments ; the dilating tissue consists of trabeculæ grown at right angles to the horse-shoe dissepiments. The dissepiments are in two regular series, an inner cylinder of horse-shoe plates, and an outer of flat, tabula-like plates ; the tabular floors are horizontal, and are usually formed of a few elongate tabellæ, occasionally of complete tabulæ.

Remarks. The character of the dissepiments is diagnostic of the genus *Trapezophyllum*. The species shows some morphological resemblance to *P. brownœ*, which has a series of horse-shoe dissepiments unusual in *Prismatophyllum* but is without the modified outer dissepiments of *Trapezophyllum*. The only other known species of the genus is the genotype, *T. elegantulum*, from the ? Lower Devonian Loyola limestone of Victoria.

Genus **Phillipsastræa** d'Orbigny ; Hill, 1939*b*, p. 236.

Phillipsastræa maculosa sp. nov. (Pl. III, figs. 5*a*, 5*b*.)

Holotype. S.U. 7268, S.U. Collection, Sulcor Quarry, Pors. 88 and 115, Par. Burdekin, near Attunga. ? Lower Couvinian.

Diagnosis. Astræoid or partly thamnastræoid *Phillipsastræa* with tabularia about 3 mm. wide and 10-15 mm. apart from axis to axis, surrounded by a zone of thickened septa about 2 mm. wide, and by a peripheral zone wherein the septa are thin and irregularly carinate ; the dissepimentarial floors are arched in the zone of thickened septa, but are declined to the periphery outside this ; the tabular floors are horizontal.

Description. The corallum is astræoid or thamnastræoid, the common wall between corallites being absent, and is large ; the corallites are from 10 to 15 mm. apart from axis to axis, while the tabularium of each corallite is about 3 mm. wide. There are 16 or 18 septa of each order ; the major septa either stop just inside the tabularium, when they are but little longer than the minor, or extend almost to the axis, either as laminæ or as discrete trabeculæ ; these extended parts are usually somewhat curved or wavy. The septa are dilated in a zone about 2 mm. wide just outside the tabularium, but outside this zone they proceed to meet those of neighbouring corallites as thin, irregularly carinate plates ; they are either continuous from corallite to corallite, or terminate against a dissepiment in the interseptal loculus of a neighbour. The dissepiments are small and globose, and geniculate in transverse or tangential sections of the corallite ; the dissepimentarial floors are arched in the zone of septal dilatation, but sag into the areas of junction of corallites. The tabular floors are horizontal, and are formed either of complete tabulæ or of a few flattened tabellæ.

Remarks. The specimen from the ? Lower Devonian Loyola limestone of Victoria, figured by Hill (1939*b*, pl. XVI, figs. 3, 4 only) as *Phillipsastræa speciosa* is more similar morphologically to our new species than to the type specimen of *P. speciosa*, and is herein transferred to the new species, although the dimensions of the corallites in the Victorian specimen are generally smaller. The age suggested is Devonian, at an horizon near that of the ? Lower Devonian Loyola limestone.

Phillipsastræa linearis sp. nov. (Pl. III, figs. 6*a*, 6*b*.)

Holotype. S.U. 7266, Sydney University Collection, Sulcor Quarry, Pors. 88 and 115, Par. Burdekin, near Attunga. ? Lower Couvinian.

Diagnosis. Astræoid or partly thamnastræoid *Phillipsastræa* with tabularia about 7 mm. apart from axis to axis, and 2 mm. in diameter, surrounded by a zone about 1½ mm. wide in which the 10 or 12 septa of each order are radially arranged ; in the peripheral parts of the corallites many of the septa are sharply curved to meet or interdigitate with those from neighbours.

Description. The corallum is astræoid or thamnastræoid, and the corallites are from 5 to 10 mm. apart from axis to axis. The tabularium of each corallite is about 2 mm. in diameter, and the septa, of which there are from 10 to 12 of each order, either all end just inside the tabularium or else the major septa extend to or towards the axis, either as continuous laminæ or discrete trabeculæ.

They are radially arranged in a zone about 1½-2 mm. wide outside the tabularium, but then curve more or less sharply to be confluent with or interdigitate with those of neighbours. The dissepimentarial floors are arched in the zone of radial arrangement of the septa, but sag between corallites ; the dissepiments are small, globose in longitudinal section of the corallum, but geniculate more often than curved in transverse sections. The tabular floors are horizontal, or slightly domed, and are formed of complete tabulæ or of several arched or flattened tabellæ.

Remarks. The specimen from the ? Lower Devonian of Loyola, Victoria, figured Hill (1939*b*, pl. XVI, figs. 5, 6 only) as *Phillipsastræa* sp. ind. probably belongs to this new species, although it differs in the absence of a marked zone of septal radiality, and in having septa minutely wavy instead of parallel-sided. The age indicated is Devonian, near the horizon of the ? Lower Devonian Loyola limestone.

Phillipsastræa carinata Hill, 1942, p. 16. (Pl. III, fig. 7.)

One specimen, S.U. 7249, from east of Sulcor Quarry, Pors. 88 and 115, Par. Burdekin, near Attunga, shows a transverse section identical with that of the type specimen from the Coblenzian Mt. Etna limestone of Queensland.

Phillipsastræa aperta sp. nov. (Pl. II, figs. 7*a*, 7*b*.)

Holotype. 7289, Sydney University Collection, Por. 50, Par. Curra, west side of Bell R., opposite Wellington Caves, N.S.W.

Diagnosis. Astræoid *Phillipsastræa* with widely spaced and but slightly thickened septa, with numerous small globose dissepiments, and with elongate tabellæ arranged on slightly domed tabular floors.

Description. The corallum is massive, the corallites are sub-equal, from 12 to 15 mm. in diameter, and fairly regularly arranged. The septa of neighbouring corallites abut on one another ; they are straight in course, and are slightly thickened in the middle third of their length ; the major septa extend nearly to the axis, one septum, or two opposite septa being longer than the others and meeting or almost meeting at the axis. The minor septa extend more than three-quarters of the way from the periphery to the axis of the corallite. There are 19 or 20 septa of each order. The tabular floors are slightly arched and are formed of elongate tabellæ closely spaced. The dissepiments are small and globose ; those about half-way between periphery and tabularium are horizontally based, but series outside and inside this slope gently down from it.

Remarks. In the equality of the corallites and the comparative delicacy and openness of the tissue, this species resembles *Radiastræa arachne* Stumm, particularly the specimen figured by Merriam (1940, pl. 13, fig. 5) from the base of the Middle Devonian of the Nevada Formation, but it does not show the aulos described for this genus by Stumm (1937, p. 439). A specimen, 6199, S.U. Collection, has been collected from the Loomberah limestone, Por. 23, Par. Loomberah, Tamworth district, N.S.W.

Phillipsastræa callosa sp. nov. (Pl. II, figs. 6*a*, 6*b*.)

Holotype. S.U. 6194, Por. 23, Parish of Loomberah, Loomberah limestone.

Diagnosis. Partly aphroid *Phillipsastræa* with septa dilated and in contact laterally in zones of irregular horizontal and vertical extent.

Description. The corallum is partly aphroid, the corallites being in contact by their dissepimentaria, and partly thamnastræoid with the septa of neighbouring corallites confluent. The tabularia are spaced from 8 to 10 mm. apart from axis to axis, and are about 2 mm. in diameter. There are 12 or 13 septa of each

order in the corallites ; they may extend only 1 mm. outside the tabularia, or may proceed to meet those of neighbouring corallites, there being no great regularity in the length. The major septa extend unequally into the tabularium, interdigitating at the axis. The thickening of the septa is characteristic of the species. It is very marked at different heights in the corallum, each horizon being a variable distance apart, and of variable lateral extent. When a transverse section cuts through one of these horizons, the septa may be so dilated as to be in contact laterally, filling the interseptal loculi, and extending far over the surface of the dissepimentarial floor at such horizons, where the corallum is usually thamnastræoid. The greatest thickness of such an horizon as seen in vertical section of the corallum is about 1 mm. The septal nature of this thickening is apparent, for it can be seen to be formed of numerous trabeculæ. In other horizons, between such dilated zones, the septa are much thinner, and are usually not developed in the peripheral parts of the corallites, so that the corallum is usually aphroid. The dissepiments are small and numerous and, as described above, often carry the thickened lateral extensions of the septa. The tabulæ are small, shallowly concave and close. The dissepimentarial floors are arched just at the tabularial margins, but sag between the tabularia.

Remarks. The irregular thickening of this species appears characteristic, though only two specimens, both from the same locality, have been examined. The arrangement of the trabeculæ in the septa appears to be not quite characteristic of the genus, but pending the discovery of richer material it seems best to include the species in *Phillipsastræa*. No comparable species is known elsewhere.

Family **Endophyllidæ** ; Hill, 1942, p. 251.

Genus **Endophyllum** Edwards and Haime ; Hill, 1942, p. 251.

Endophyllum cf. **abditum** Edwards and Haime. (Pl. II, figs. 8*a*, 8*b*.)

One specimen, 6196, S.U. Collection, from the Loomberah limestone in Por. 23, Par. Loomberah, on the west bank of Sandy Ck., is comparable with the English cerioid species described by Edwards and Haime (1853, p. 233, pl. LII, fig. 6) and Jones (1932, p. 87, pl. X, figs. 3, 4). The corallites are large, polygonal but somewhat elongate in transverse section, the longer diameter being about 30 mm. and the shorter 20 mm. There are about 24 major septa, which extend half-way or more across the tabularium, and alternating minor septa extend to the edge of the tabularium. The major septa are usually slightly curved near their axial edges, but the curvature is not regular in the only two corallites examined. The septa are thickened and in contact at their bases, and are lonsdaleoid, i.e. discontinuous through the large dissepiments ; the crests on these lonsdaleoid dissepiments are also thickened, so that those of neighbouring septa are in contact. The tabularium is about half as wide as the corallite ; the tabulæ are tall close domes with upturned edges, their regularity somewhat broken by the axial parts of the septa. The dissepiments are steeply inclined, those of the outer series are lonsdaleoid and very large, bearing the dilated septal crests ; those of the inner series are small and unthickened.

Remarks. The corallum differs from figured specimens of the English species in having fewer and thicker septa with great dilatation over the surfaces of the lonsdaleoid dissepiments. In Europe the species is broadly Middle Devonian ; in Asia it is Lower Middle Devonian. A variety occurs in the Givetian Burdekin limestones in Queensland.

Genus **Sanidophyllum** Etheridge, 1899, p. 154.

Genotype. *Sanidophyllum davidis* Etheridge, 1899, p. 154, pl. XVI, XVII, fig. 1 ; XIX, fig. 7 ; XX, figs. 4 and 5 ; and XXXVIII, fig. 2. Moore Ck. limestone, " Moore Ck., 1 mile north of Tamworth ".

Diagnosis. Compound Rugosa with periodic rejuvenescence ; the cylindrical corallites have a narrow peripheral stereozone without dissepiments ; periodically the stereozone of each corallite expands into a liliiform calice, and meets the expansions from others, so that the periodically succeeding calical surfaces are like those of a cerioid corallum ; rejuvenescence rapidly occurs, and a corallite of normal diameter grows from each calice straight up for some distance, and then expands again into a liliiform calice ; the major septa may be long, meeting at the axis, where they may be vortically rotated ; the minor septa do not extend beyond the stereozone ; the tabulæ are flattened domes, which sometimes sag axially.

Remarks. The growth form of *Sanidophyllum* is similar to that made familiar to students by Lambe's (1901) figures of *Eridophyllum colligatum* ; with the difference that whereas the lateral calical expansions have dissepiments in the Canadian species, in the Australian genus the expansions are of a peripheral stereozone without dissepiments. The genus has been referred to the Endophyllidæ ; but the complete absence of lonsdaleoid dissepiments may indicate that its affinities are elsewhere. It may perhaps belong to the Mycophyllidæ, which have a peripheral stereozone without dissepiments, and liliiform calices in some species ; but the septa of the Mycophyllidæ are amplexoid, and are formed of closely spaced Naic plates not seen in *Sanidophyllum*. Or it may be related to the Silurian genus *Codonophyllum*, which indeed has trochoid and sometimes liliiform calices, domed tabular floors and a peripheral stereozone without dissepiments, but is without the regular rejuvenescence of our genus, whose septal structure again is not of the type seen in *Codonophyllum*. It seems that the affinities of *Sanidophyllum* may be determined when our knowledge of septal structure increases ; but in the meantime it is left somewhat doubtfully in the Endophyllidæ.

Sanidophyllum davidis Etheridge. (Pl. IV, fig. 10.)

Sanidophyllum davidis Etheridge 1899 p. 154, pls. XVI ; XVII, fig. 1 ; XIX, fig. 7 ; XX, figs. 4, 5 ; XXXVIII, fig. 2. " Moore Ck., 1 mile north of Tamworth ". Moore Ck. limestone.

Type Material. Untraced, possibly in Australian Museum.

Diagnosis. Sanidophyllum in which the cylindrical corallites are distant, the calical expansions are nearly horizontal, the peripheral stereozone of the cylindrical portion is narrow, and the septa are typically withdrawn from the axis.

Description. The corallum is very large, with periodic rejuvenescence ; the corallites are cylindrical and distant, but periodically all of them have calical expansions ; those from neighbours joining, so that a cerioid calical platform results. The cerioid platforms rise steeply from the cylindrical parts at first, but then turn outwards more or less sharply to form practically horizontal platforms. The individual corallites are from 10 to 20 mm. in diameter in their cylindrical parts, but the cerioid parts, at the positions of the calical expansions, may be up to 40 mm. in diameter. The cylindrical parts are epithecate and vary in distance apart, usually from 12 to 22 mm., and the vertical distance between the calicular platforms is from 8 to 25 mm. In the cylindrical parts of the corallites there is a very narrow peripheral stereozone formed by the dilatation of the bases of the septa ; there are from 25 to 28 septa of each order, the minor being extremely short, mere bases on the wall, and the major being typically very short, about 2 mm. long, although occasionally they may extend almost to the axis ; when this occurs they are usually straight, though in some cases a slight rotation of the axial ends may be observed. The tabular floors

are flat topped or sagging domes, and are formed either of complete tabulæ or of tabellæ, the latter often reinforcing the margins of the flat top of the dome. There are no dissepiments.

Remarks. There is an error in the locality given by Etheridge, for it is Springs Ck., and not Moore Ck., which is 1 mile north of Tamworth. As *Sanidophyllum* is unknown elsewhere, the species is of no assistance in determining the age of the Moore Ck. limestone.

Localities. Moore Ck., Springs Ck., in S.W. corner of Por. 264, Par. Burdekin.

Sanidophyllum colligatum (Etheridge). (Pl. IV, figs. 11, 12.)

Endophyllum schluteri var. *colligatum* Etheridge, 1920, p. 55, pl. XIII, figs. 1, 2. Moore Ck. limestone, Moore Ck. (D. A. Porter).

Type Material. Whereabouts at present unknown.

Diagnosis. Sanidophyllum with corallites very close together and with narrow, rather highly inclined and dilated calical expansions, with a wider peripheral stereozone than in the type species, and with more and longer septa, which typically extend to the axis and are slightly rotated vortically there.

Description. The corallum is very large, and consists of alternating cylindrical and cerioid calical portions, repeated by rejuvenescence which is simultaneous in all corallites in the corallum. The individual corallites may be as wide as 25 mm. in their cylindrical parts, and 30 mm. at the cerioid junctions of their calical expensions. The expanded calical margins are about 2 mm. thick from epithecal surface to upper surface, and are 5 mm. or more apart. They rise steeply from the cylindrical portion to meet one another at an acute angle. The cylindrical parts of the corallites are fairly close together, e.g. from 0 to 4 mm. There are from 30 to 33 septa of each order, each dilated at the periphery to form a stereozone about 2 mm. wide ; the minor septa proceed but little inside this stereozone, but the major septa usually extend to the axis, where they may be rotated vortically ; they are much thinner inside the peripheral stereozone, though there may be some dilatation near the axis. There are no dissepiments at all. The tabular floors are domes or flattened domes with upturned edges. They may consist of complete tabulæ, or of elongate tabellæ.

Remarks. Although the type material is at present unavailable, I am satisfied that the figures given by Etheridge show that the form which he considered to be a variety of *Endophyllum schluteri* is really a species of *Sanidophyllum.* Nowhere in the figures can any trace of lonsdaleoid dissepiments, so characteristic of *Endophyllum*, be found. The expansions from the cylindrical parts of the corallites are in all cases calical stereozones, as in *Sanidophyllum*, and not dissepimental tissue, as in *Endophyllum.* The cylindrical parts of the corallum in *Endophyllum* are merely tabularia, while in *Sanidophyllum* and in Etheridge's *E. colligatum* they are the sub-calical parts of the corallite and contain the whole lumen. The species differs from *S. davidis* in the greater width of the cylindrical parts, the greater thickness and closeness and higher inclination of the lateral expansions, the greater width of the stereozone and the greater number of septa. No comparable species is known elsewhere, so it does not assist in age determination.

Localities. Moore Ck. ; limestone in Por. 127, Par. Burdekin ; in central eastern part of Por. 264, Par. Burdekin ; in central eastern part of Por. 249, Par. Burdekin. All Moore Ck. horizon.

Family **Entelophyllidæ**; Hill, 1940*b*, p. 410.

Genus **Eridophyllum** Edwards and Haime; Hill, 1940*c*, p. 270.

Eridophyllum bartrumi Allan; Hill, 1940*c*, p. 271. (Pl. III, figs. 8*a*, 8*b*.)

There are a large number of coralla of rather regular phaceloid growth, with stout corallites, from the Sulcor Quarry in Pors. 88 and 115, Par. Burdekin, near Attunga, which have the internal structure of *E. bartrumi*; the spacing of the plates is however a little more open and regular than in the typical specimens, and it may be that the Attunga forms represent a local variant, although they are not herein separated from the species. The species is now known from the Lower Middle Devonian of New Zealand, from the Murrumbidgee and Goodradigbee limestones and from the Couvinian limestones near Geurie, in the Wellington district, and from the Tamworth Province in the Sulcor limestone, while there is a very closely similar species from the lower part (see Merriam, 1940, p. 9) of the Middle Devonian Nevada limestone of the U.S.A., namely *Disphyllum occidens* Stumm (1938, pl. 59, fig. 3).

Family **Favistellidæ**; Hill, 1939*b*, p. 240.

Genus **Favistella** Hall; Hill, 1939*b*, p. 240.

Favistella cf. **rhenana** (Frech). (Pl. IV, fig. 13.)

A single transverse section (S.U. 7258) resembling *F. rhenana* as described by Hill (1942, p. 253) from the Givetian Burdekin limestones of north Queensland, has been sent to me from the limestone in Por. 264, Par. Burdekin, near Attunga. It differs from the Queensland material only in having 24 as against a maximum of 20 septa of each order. The horizon is probably that of the Moore Ck. limestone.

Favistella neminghensis (Etheridge). (Pl. II, figs. 4*a*, 4*b*.)

Columnaria neminghensis Etheridge, 1918, p. 50, pl. VIII, pl. IX, Por. 181, Par. Nemingha, Co. Parry, Tamworth District; Lower Limestone of series (i.e., probably Nemingha Limestone).

Holotype (by monotypy). Australian Museum 903 (from Mines Dept., N.S.W. specimen 5099).

Diagnosis. Cerioid *Favistella* with corallites about 3 mm. in diameter, with typically twelve major septa extending to the axis, where their axial edges are turned aside, very short minor septa and flat tabulæ with down-turned edges.

Description. The corallum is cerioid and mushroom shaped, the type (the only specimen known) measuring 16 cm. $\times 12 \cdot 5$ cm. The corallites are straight and five- or six-sided, with moderately thick walls, and are of an average diameter of 3 mm., although corallites of 4 mm. occur. There are typically 12 major septa which are thin axially, but thicken slightly wedge-wise to the periphery, where their dilated bases are in contact with those of the minor septa to form the wall. They are long, reaching to the axis, where their axial ends are turned aside irregularly, and interdigitate with one another. The minor septa are very short or sometimes do not appear. There are no dissepiments. The tabulæ are complete, parallel and rather distant, being horizontal with down-turned margins. The individual trabeculæ of the septa may be traced in suitable longitudinal sections.

Remarks. The species has fewer septa (12 as against 18) than the Middle Devonian *F. devonica* (Schluter) from the Eifel, and the Upper Silurian *F. gotlandica* (Edwards and Haime).

Family **Mictophyllidæ**; Hill, 1940*c*, p. 264.

Genus **Mictophyllum** Lang and Smith; Hill, 1939*b*, p. 246; 1940*c*, p. 265.

Mictophyllum cf. **cresswelli** (Chapman). (Pl. III, fig. 9.)

Large individuals (S.U. 7247, 7285) occur in the Sulcor Limestone, in Pors. 88 and 115, Par. Burdekin, near Attunga, with diameters from 40 to 55 mm. There are 51 major and 51 minor septa; the minor septa extend about half-way to the axis, and the major extend somewhat unequally to the axis, with some slight curvature, and with slightly unequal interseptal loculi. The septa are a little dilated in the dissepimentarium, the dilatation increasing towards the periphery, although in the same direction the dilatation tends to become replaced by numerous small lateral dissepiments. The dissepiments are numerous, small and close, and many are geniculate in transverse section of the corallum. The tabularium is wide, equal to about half the diameter of the corallum, and the tabular floors are domes with upturned margins, formed by rather large tabellæ.

Remarks. The specimens differ from typical *M. cresswelli* (Chapman; Hill, 1939*b*, p. 246) from the Lower or Middle Devonian limestone of Lilydale in Victoria in the larger number of septa, and in the absence of sections of the early stages, we do not know whether the characteristic peripheral stereozone of the early stages of *M. cresswelli* is present in the Attunga specimens. They differ from the lower Middle Devonian *M. trochoides* of the Murrumbidgee formation in the type of septal dilatation in the mature corallum.

Family **Mycophyllidæ**; Hill, 1940*a*, p. 156.

Genus **Pseudamplexus** Weissermel; Hill, 1940*a*, p. 157.

Pseudamplexus princeps (Etheridge); Hill and Jones, 1940, p. 185.

One specimen, S.U. 7247, from the Sulcor limestone in Por. 115, Par. Burdekin, near Attunga, is placed in this Lower and Lower Middle Devonian species.

Family **Pycnactidæ**; Hill, 1940*b*, p. 401.

It seems very likely that the two genera *Hallia* Edwards and Haime and *Aulacophyllum* Edwards and Haime, as interpreted by Sloss (1939, p. 63) are members of the Pycnactidæ, as they have the septal dilatation lasting longer in the tabularium than in the dissepimentarium, and in the cardinal quadrants longer than in the counter; while the cardinal septum may sometimes be very long in *Hallia*; the tabulæ of their type species have not been adequately described.

Genus **Aulacophyllum** Edwards and Haime.

Stewart, 1938, p. 29, Columbus (? Couvinian) limestone of Ohio.

Sloss, 1939, p. 63, transverse limestone of Michigan, ? Givetian.

Genotype. *Aulacophyllum sulcatum* (d'Orbigny), Falls of Ohio.

Diagnosis. Solitary Rugosa with long septa with septal dilatation in the tabularium reduced from the axis outwards and from counter to cardinal quadrants, and with the septa of the cardinal quadrants curved towards the cardinal fossula.

Remarks. The genus is insufficiently understood, as we have no good descriptions or figures of the tabular floors or tabellæ. In America it occurs in the Middle Devonian, in the ? Couvinian Columbus limestone and the ? Givetian Traverse limestone. No authentic occurrences of the genus in Europe are known

to me. The Silurian European species placed in the genus by Edwards and Haime, *Hippurites mitratus* Schlotheim, *partim*, is a species of *Pycnactis*.

Aulacophyllum trizonatum sp. nov. (Pl. III, figs. 10, 11, 12.)

Holotype. S.U. 7245, Sulcor limestone, Por. 88, Par. Burdekin, near Attunga, Tamworth. ? Lower Couvinian.

Diagnosis. *Aulacophyllum* with a narrow axial zone containing the curved axial ends of a few major septa which are longer than the others, with about 50 septa of each order at a diameter of 50 mm., and with broadly domed tabulæ.

Description. The corallum is large, curved and trochoid, the greatest diameter observed being 50 mm. There are 45 to 50 septa of each order. In early stages the dissepimentarium is narrow, only 3 mm. wide at 30 mm. diameter, while the tabularium is 25 mm. The major septa are long, and most of them stop equally short of the axis, some few proceeding with irregular curvature into the narrow axial space thus formed; they are so dilated that the tabularium is completely filled; the outer parts of the septa in the tabularium are somewhat recrystallised, in the manner characteristic of *Pycnactis*. In older stages the dissepimentarium widens, up to 13 mm. when the tabularium is 30 mm. in diameter; the septa lose their great dilatation, except in a zone about 8 mm. wide around the outer cardinal parts of the tabularium; the axial space containing the few irregularly curved long septal ends persists. In all stages the septa of the cardinal quadrants are curved towards the cardinal fossula. The cardinal septum is shorter than the rest. The dissepiments are rather large and distant, and some are geniculate in transverse section of the corallum. They are steeply inclined and rather flat. The tabular floors are broadly domed, with an axial depression, and consist of large tabellæ.

Remarks. None of the American Middle Devonian species is very close to this Australian form.

Family **Rhabdocyclidæ**; Hill, 1940*b*, p. 404.

Genus **Tryplasma** Lonsdale; Hill, 1940*b*, p. 405.

Tryplasma sp.

A phaceloid corallum, S.U. 6242, with corallites 3-4 mm. in diameter occurs in Por. 192, Par. Attunga, on the west side of Boundary Creek, north of Moore Creek, in a limestone correlated by Dr. Ida Brown with the Nemingha. The septa are short and acanthine, the tabulæ horizontal and distant, and there are no dissepiments. The age suggested is pre-Middle Devonian.

? **Tryplasma** sp. (Pl. IV, fig. 14.)

Fragments of cylindrical corallites occur in S.U. 7186 from Por. 252, Par. Burdekin, in Follington's limestone, which is correlated with the Givetian Moore Ck. limestone. The corallites are about 15 mm. in diameter, and bear very short septa, 1·5 mm. long, each consisting of a single series of discrete trabeculæ, growing upwards at a very slight angle from the horizontal. It cannot be ascertained, however, whether the trabeculæ are rhabdacanths, as in unaltered *Tryplasma*, or whether they are holacanths set in lamellar sclerenchyme, as is found when recrystallisation has affected *Tryplasma*. For this reason, and because *Tryplasma* is not elsewhere known above the top of the Lower Devonian, the specimen is only doubtfully placed in the genus. The tabulæ are complete, and distant, about 4 mm. apart.

Family **Spongophyllidæ**; Hill, 1939*a*, p. 58; 1942, p. 254.

Genus **Spongophyllum** Edwards and Haime, Hill, 1939*a*, p. 60.

Spongophyllum giganteum Etheridge. (Pl. IV, figs. 15*a*, 15*b*.)

Etheridge, 1899, p. 158, pl. XX, figs. 1-3; XXXVIII, fig. 3. Moore Ck. limestone, Moore Ck.

Jones, 1932, p. 54, text-fig. 1.

New localities for this species are: north part of Por. 252, Par. Burdekin; N.E. part of Por. 248 (probably 232), Par. Burdekin; and S. of Moore Ck. All are considered to be equivalent to the Moore Ck. limestone. In the specimen S.U. 7235 from Por. 248 (probably 232), the corallites are smaller than is typical, being only 10 mm. in diameter or less, and having rather fewer septa than the types, only 17 of each order being counted as against the 20 to 25 previously described, while the lonsdaleoid portion of the dissepimentarium is very narrow or even absent in parts. Nevertheless it seems that this specimen is a member of the species, for in S.U. 7161 from the north part of Por. 252, similar small corallites occur with the typical larger ones with wide dissepimentaria.

Spongophyllum halysitoides Etheridge; Hill, 1940*a*, p. 162. (Pl. II, figs. 5*a*, 5*b*.)

The type specimen, Australian Museum 187, F 16453, is from the Nemingha limestone, road near Beedle's Farm, Moonbi, Co. Inglis, N.S.W. Another specimen, A.M. 206 (F 6760) is labelled as from Moore Ck., near Tamworth, collected by D. A. Porter in 1900. This record suggests that limestones of Nemingha horizon outcrop on Moore Ck., as well as those of typical Moore Ck. horizon.

Spongophyllum ? immersum Hill, 1942, p. 254.

S.U. 7159 from the Moore Ck. limestone in the south end of Por. 137, Par. Woolomol, and S.U. 7154 from Por. 61, Par. Woolomol, are phaceloid coralla which from the width of the corallites and the presence of a border of lonsdaleoid dissepiments appear to be referable to this species, but preservation is so poor that the arrangement of the axial septal ends cannot be discerned. The species is known elsewhere only from the Givetian Burdekin Downs limestone of Queensland.

Stringophyllum bipartitum Hill, 1942, p. 261. (Pl. IV, fig. 17.)

Two specimens (S.U. 7191, 7195) from the limestone in Por. 127, Par. Burdekin, near Attunga, N.S.W., are of a phaceloid species, the individual corallites of which are indistinguishable from those of *Stringophyllum bipartitum*, except that the minor septa are somewhat more frequently developed as continuous plates rather than septal crests, than in the Queensland specimens. It thus seems that *S. bipartitum* is really a phaceloid species, as was suspected from the association of specimens in the Queensland limestone. In Queensland it occurs in the Givetian Burdekin Downs limestone, and the N.S.W. occurrence is in a limestone correlated with the Givetian Moore Ck. limestone.

Stringophyllum densum sp. nov. (Pl. IV, fig. 16.)

Holotype. S.U. 7193, Por. 127, Par. Burdekin, north of Sulcor Quarry, near Attunga; Givetian.

Diagnosis. Phaceloid *Stringophyllum* with slender corallites with a wide peripheral stereozone which may be replaced sporadically by lonsdaleoid dissepiments.

Description. The corallum is phaceloid, but the only specimen known has been considerably battered, so that the corallites are lying irregularly in the matrix. They are about 5 mm. in average diameter. There are about 12 or 14 septa of each order, which are dilated and in contact peripherally and consist of discrete trabeculæ axially. Frequently the peripheral stereozone may be suppressed, on the appearance of a series of large lonsdaleoid dissepiments; or sometimes the minor septa may be suppressed, and large dissepiments develop between the major septa. The minor septa do not extend so far towards the axis as the major, but it is frequently difficult to distinguish them. There is often a single series of large lonsdaleoid dissepiments, and the tabulæ are complete, concave plates.

Remarks. The peripheral stereozone is unknown in any other species of *Stringophyllum*, which genus is characteristic of the Middle Devonian, particularly of the Givetian.

Acknowledgments.

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References.

Benson, W. N., 1918. The Geology of the Loomberah District and a Portion of the Goonoo Goonoo Estate. *Proc. Linn. Soc. N.S.W.*, **43**, pp. 320-394, pls. XXXI-XXXVIII, and 5 text-figs.

Brown, I., 1942. The Tamworth Series (Lower and Middle Devonian) near Attunga, N.S.W., *J. Proc. Roy. Soc. N.S.W.*, **76**, pp. 165-176.

Carne, J. E., and Jones, L. J., 1919. The Limestone Deposits of New South Wales. *Geol. Surv. N.S.W. Mineral Resources*, No. 25.

Dun, W. S., 1918. Notes on the Loomberah Fossils, pp. 375-384, pls. XXXIV-XXXVIII, in Benson, 1918.

Edwards, H. M., and Haime, J., 1853. British Fossil Corals. Part IV. *Palæontogr. Soc. Monogr.*, pp. 211-244, pls. XLVII-LVI.

Etheridge, R., Jnr., 1890. On the Occurrence of the Genus *Tryplasma* Lonsdale (*Pholidophyllum* Lindstrom) and another Coral apparently referable to *Diphyphyllum* Lonsdale, in the Upper Silurian and Devonian Rocks respectively, of N. S. Wales. *Rec. geol. Surv. N.S.W.*, **2**, pp. 15-21, pl. I.

———— 1899. On the Corals of the Tamworth District, Chiefly from the Moore Ck. and Woolomol Limestones. *Rec. geol. Surv. N.S.W.*, **6**, pp. 151-182, pls. XVI-XXXVIII.

———— 1918. Two Remarkable Corals from the Devonian of New South Wales (*Spongophyllum halysitoides* and *Columnaria neminghensis*). *Rec. Aust. Mus.*, **12**, pp. 49-51, pls. VII-IX.

———— 1920. Further Additions to the Coral Fauna of the Devonian and Silurian of New South Wales (*Endophyllum schluteri* var. *colligatum*, *Columnopora* (*Gephuropora*) *Duni*, *Vepresiphyllum falciforme*, and *Syringopora trupanonoides*. *Rec. geol. Surv. N.S.W.*, **9**, pp. 55-63, pls. XIII-XV.

Frech, F., 1886. Die Cyathophylliden und Zaphrentiden des deutschen Mitteldevon. *Palæont. Abh.* III, Heft. 3, 119 pp., 8 pls.

Hill, D., 1939*a*. The Middle Devonian Rugose Corals of Queensland. I. Douglas Ck. and Drummond Ck., Clermont District. *Proc. Roy. Soc. Queensl.*, **50**, pp. 55-64, pls. IV, V.

———— 1939*b*. The Devonian Rugose Corals of Lilydale and Loyola, Victoria. *Proc. Roy. Soc. Vict.* (N.S.), **51**, pp. 219-256, pls. XIII-XVI.

———— 1939*c*. The Carboniferous Rugose Corals of Scotland. Part II. *Palæontogr. Soc. Monogr.*, pp. 79-114, pls. III-V.

Hill, D., 1940*a*. The Middle Devonian Rugose Corals of Queensland. II. The Silverwood—Lucky Valley Area. *Proc. Roy. Soc. Queensl.*, **51**, pp. 150-168, pls. II, III.
——— 1940*b*. The Silurian Rugosa of the Yass-Bowning District, N.S.W. *Proc. Linn. Soc. N.S.W.*, **65**, pp. 388-420, pls. XI-XIII.
——— 1940*c*. The Lower Middle Devonian Rugose Corals of the Murrumbidgee and Goodradigbee Rivers, N.S.W. *J. Proc. Roy. Soc. N.S.W.*, **74**, pp. 247-276, pls. IX-XI.
——— 1942. The Middle Devonian Rugose Corals of Queensland. III. Burdekin Downs, Fanning R., and Reid Gap, North Queensland. *Proc. Roy. Soc. Queensl.*, **53**, pp. 229-268, pls. V-XI.
——— 1942. The Lower Devonian Rugose Corals from the Mt. Etna Limestone, Qld. *Proc. Roy. Soc. Queensland*, **54**, pp. 13-22, pl. I.
Hill, D., and Jones, O. A., 1940. The Corals of the Garra Beds, Molong District, N.S.W. *J. Proc. Roy. Soc. N.S.W.*, **74**, pp. 175-208, pls. II-VIII.
Jones, O. A., 1929. On the Coral Genera *Endophyllum* Edwards and Haime and *Spongophyllum* Edwards and Haime. *Geol. Mag. Lond.*, **66**, pp. 84-91, pl. X.
——— 1932. A Revision of the Australian Species of the Coral Genera *Spongophyllum* E. and H. and *Endophyllum* E. and H. with a Note on *Aphrophyllum* Smith. *Proc. Roy. Soc. Queensl.*, **44**, pp. 50-63, pls. III, IV.
Lambe, L. M., 1901. A Revision of the Genera and Species of Canadian Palæozoic Corals. The Madreporaria Aporosa and the Madreporaria Rugosa. *Contr. Canad. Palæont.*, **4**, pp. 97-197, pls. VI-XVIII.
Lang, W. D., and Smith, S., 1935. *Cyathophyllum cæspitosum* Goldfuss, and other Devonian Corals considered in a Revision of that Species. *Quart. J. geol. Soc. Lond.*, **91**, pp. 538-590, pls. XXXV-XXXVII.
Loewe, S., 1914. Die devonischen Korallen von Ellesmereland. Inaug. Dissert. Univ. Breslau, and Report of the Second Norwegian Arctic Expedition in the Fram, 1898-1902, No. 30, 23 pp., 7 pls.
Merriam, C. W., 1940. Devonian Stratigraphy and Palæontology of the Roberts Mountains Region, Nevada. *Geol. Soc. Amer., Special Pap.* No. 25, 114 pp., 16 pls.
Sloss, L. L., 1939. Devonian Rugose Corals from the Traverse Beds of Michigan. *J. Paleont. Tulsa*, **13**, pp. 52-73, pls. 9-12.
Stewart, G. A., 1938. Middle Devonian Corals of Ohio. *Geol. Soc. Amer. Special Pap.* No. 8, 120 pp., 20 pls.
Stumm, E. C., 1937. The Lower Middle Devonian Tetracorals of the Nevada Limestone. *J. Paleont.*, **11**, pp. 423-443, pls. 53-55.
——— 1938. Upper Middle Devonian Rugose Corals of the Nevada Limestone. *J. Paleont.*, **12**, pp. 478-485, pls. 58, 59.

Explanation of Plates.

Plate II. Rugosa from the Nemingha and Loomberah Limestones and Equivalents.

All figures ×1·2 diameters approximately.

Fig. 1.—*Acanthophyllum* cf. *mansfieldense* (Dun). S.U. 7254, Por. 256, Par. Burdekin. ? Nemingha equivalent. Transverse section.

Fig. 2.—*Lyrielasma floriforme* sp. nov. Holotype, S.U. 7252 limestone in middle of south boundary, Por. 227, Par. Burdekin. ? Nemingha equivalent. *a*, Transverse and *b*, vertical section.

Fig. 3.—"*Cystiphyllum*" *multitrabeculatum* sp. nov. Holotype, S.U. 7214, limestone in Por. 15, Par. Burdekin. ? Nemingha equivalent. *a*, Transverse, and *b*, vertical section.

Fig. 4.—*Favistella neminghensis* (Etheridge). Holotype, A.M. 903, F 5099, Por. 181, Par. Nemingha, Co. Parry, Tamworth District; lower limestone of series (i.e., probably Nemingha). *a*, Transverse, and *b*, vertical section.

Fig. 5.—*Spongophyllum halysitoides* Etheridge. Holotype, A.M. 187, F 16453, road near Beedle's Farm, Moonbi, Co. Inglis, N.S.W. Nemingha limestone. *a*, Transverse, and *b*, vertical section.

Fig. 6.—*Phillipsastræa callosa* sp. nov. Holotype, S.U. 6194, Por. 23, Par. Loomberah, Loomberah limestone. *a*, Transverse, and *b*, vertical section.

Fig. 7.—*Phillipsastræa aperta* sp. nov. S.U. 6199, Por. 23, Par. Loomberah, Loomberah limestone. *a*, Transverse, and *b*, vertical section.

Fig. 8.—*Endophyllum* cf. *abditum* Edwards and Haime. U.S. 6196, Por. 23, Par. Loomberah, Loomberah limestone. *a*, Transverse, and *b*, vertical section.

Fig. 9.—*Xystriphyllum mitchelli* (Etheridge). S.U. 7251, south-west corner of Por. 248, Par. Burdekin. Horizon unknown. Transverse section.

Plate III. Rugosa from the Couvinian Sulcor Limestone.

All figures ×1·2 diameters approximately.

Fig. 1.—*? Dohmophyllum* sp. S.U. 7262, Pors. 88-115, Par. Burdekin. Transverse section.

Fig. 2.—*Xystriphyllum magnum* sp. nov. Holotype, S.U. 7270, Sulcor Quarry, Pors. 88-115, Par. Burdekin. *a*, Transverse, *b*, vertical section.

Fig. 3.—*Trapezophyllum coulteri* sp. nov. Holotype, S.U. 5243, Por. 88, Par. Burdekin. *a*, Transverse, and *b*, vertical section.

Fig. 4.—*Prismatophyllum browncæ* sp. nov. S.U. 7246, Sulcor limestone, N.E. of Attunga. *a*, Transverse, and *b*, vertical section.

Fig. 5.—*Phillipsastræa maculosa* sp. nov. (*a*) Holotype, S.U. 7268, Pors. 88-115, Par. Burdekin. Transverse section. (*b*) S.U. 7269. Same locality. Vertical section.

Fig. 6.—*Phillipsastræa linearis* sp. nov. Holotype, S.U. 7266, Pors. 88-115, Par. Burdekin. *a*, Transverse, and *b*, vertical section.

Fig. 7.—*Phillipsastræa carinata* Hill. S.U. 7249, east of Sulcor Quarry, Pors. 88-115, Par. Burdekin. Transverse section.

Fig. 8.—*Eridophyllum bartrumi* (Allan). *a*, S.U. 7265, Pors. 88-115, Par. Burdekin. Transverse section. *b*, S.U. 7267. Same locality. Vertical section.

Fig. 9.—*Mictophyllum* cf. *cresswelli* (Chapman). S.U. 7247, Pors. 88-115, Par. Burdekin. Transverse section.

Fig. 10.—*Aulacophyllum trizonatum* sp. nov. Holotype, S.U. 7245, Por. 88, Par. Burdekin. Transverse section.

Fig. 11.—*Aulacophyllum trizonatum* sp. nov. S.U. 6212, Por. 88, Par. Burdekin. Transverse section, young stage.

Fig. 12.—*Aulacophyllum trizonatum* sp. nov. S.U. 7242, Pors. 88-115, Par. Burdekin. Vertical section, through calice.

Plate IV. Rugosa from the Moore Ck. Limestone and Equivalents.

All figures ×1·2 diameters approximately.

Fig. 1.—*Dohmophyllum* sp. A.M. 179, F 6199, Moore Ck. limestone in Springs Ck. *a*, Transverse, and *b*, vertical section.

Fig. 2.—"*Campophyllum*" cf. *lindstromi* (Frech). A.M.F. 6201, Springs Ck. *a*, Transverse, and *b*, vertical section.

Fig. 3.—*Mesophyllum cornubovis* (Etheridge). A.M. 883, F 16410, Attunga. Transverse section.

Fig. 4.—*Mesophyllum cornubovis* (Etheridge). A.M.F. 6798, Moore Ck., near Tamworth. Vertical section.

Fig. 5.—*Disphyllum robustum* (Etheridge). Holotype, M 571 Eth., A.M., Moore Ck. Transverse section.

Fig. 6.—*Disphyllum robustum* (Etheridge). A.M. 164, F 6184, Springs Ck. Vertical section.

Fig. 7.—*Phacellophyllum porteri* (Etheridge). A.M.F. 6149, Moore Ck. Transverse section.

Fig. 8.—*Phacellophyllum porteri* (Etheridge). A.M. 166, F 6199, Springs Ck. Vertical section.

Fig. 9.—*Disphyllum* cf. *gregorii* (Etheridge). S.U. 7263, north-east part of Por. 248, Par. Burdekin. Transverse section.

Fig. 10.—*Sanidophyllum davidis* Etheridge. S.U. 5251, Moore Ck. limestone, 2 miles south of Moore Ck. Obliquely transverse section.

Fig. 11.—*Sanidophyllum colligatum* Etheridge. S.U. 5245, Por. 264, Par. Burdekin. Transverse section.

Fig. 12.—*Sanidophyllum colligatum* Etheridge. A.M. 199, F 6161, Moore Ck. Vertical section.

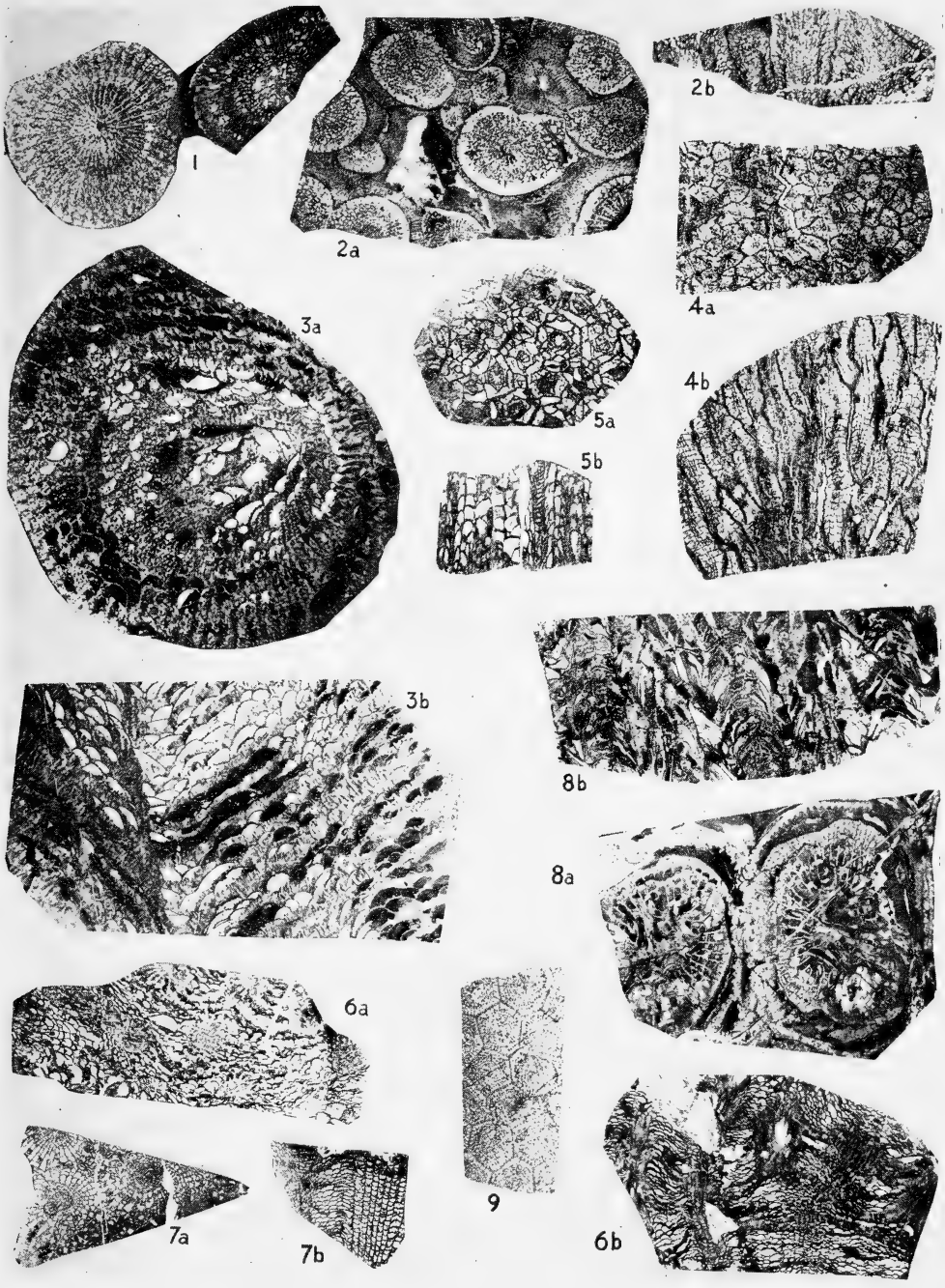
Fig. 13.—*Favistella* cf. *rhenana* (Frech). S.U. 7258, Por. 264, Par. Burdekin. Transverse section.

Fig. 14.—*? Tryplasma* sp. S.U. 7186, Por. 252, Par. Burdekin. *a*, Transverse, and *b*, vertical section.

Fig. 15.—*Spongophyllum giganteum* Etheridge. S.U. 7235, south-east part of Por. 232, Par. Burdekin. *a*, Transverse, and *b*, vertical section.

Fig. 16.—*Stringophyllum densum* sp. nov. Holotype, S.U. 7193, Por. 127, Par. Burdekin, north of Sulcor Quarry.

Fig. 17.—*Stringophyllum bipartitum* Hill. S.U. 7195, Por. 127, Par. Burdekin, near Attunga. Transverse section.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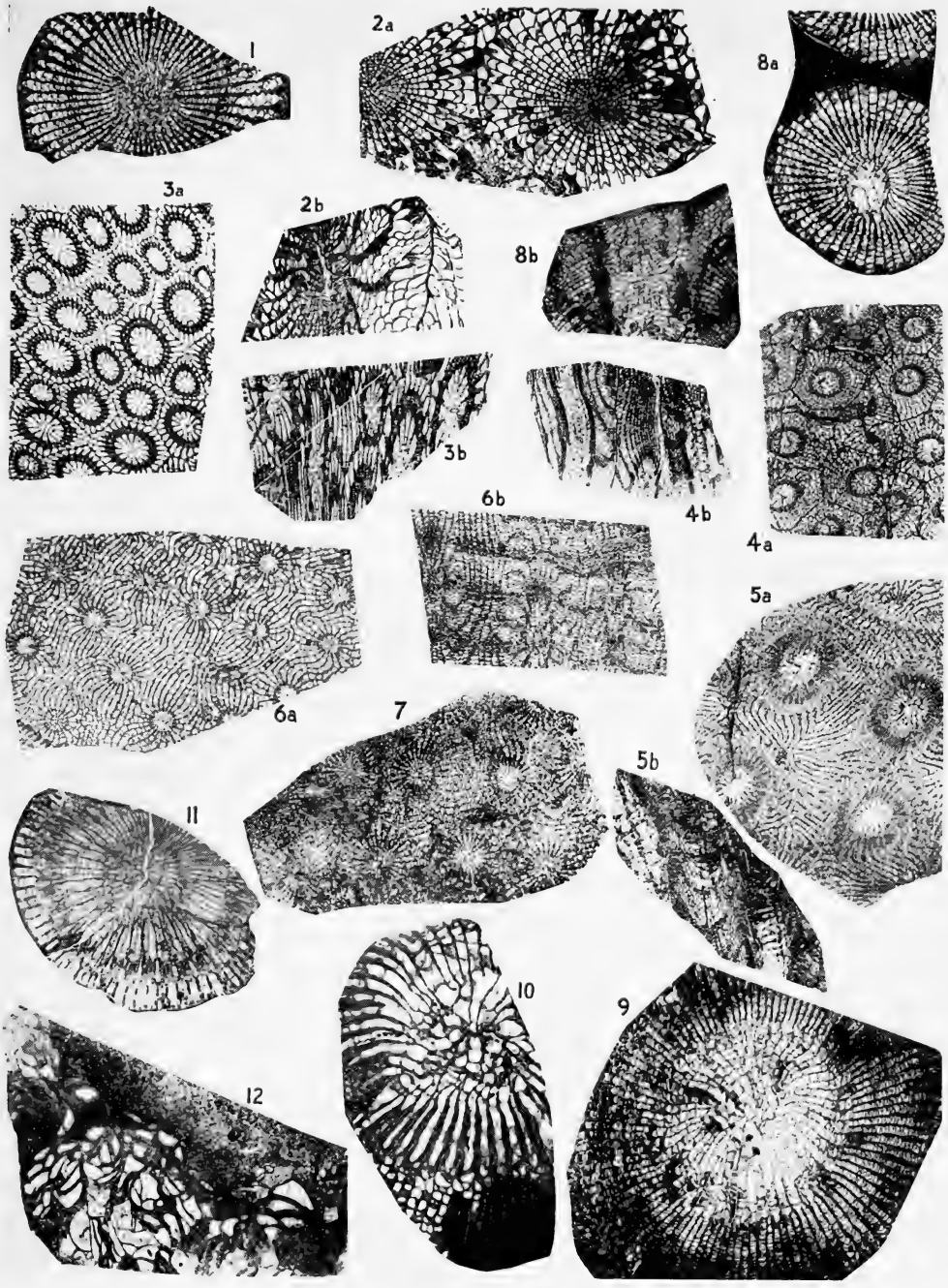
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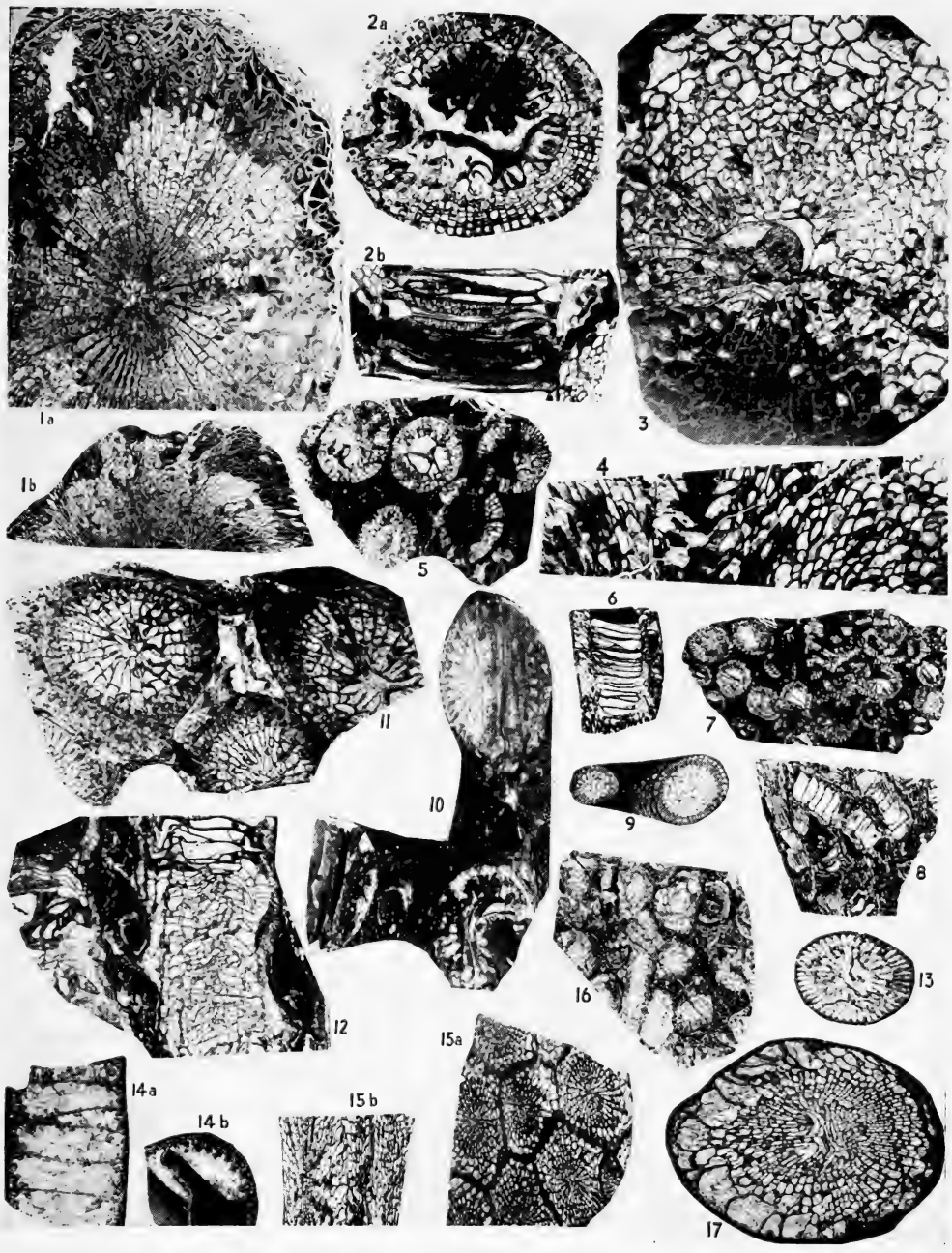
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THE TAMWORTH SERIES (LOWER AND MIDDLE DEVONIAN) NEAR ATTUNGA, N.S.W.

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With two text-figures.

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Contents.

Page
1. Introduction 165
2. Previous Investigation.. 166
3. Stratigraphy of Tamworth Series—
(*a*) Nemingha Stage 167
(*b*) Sulcor Stage 170
(*c*) Moore Creek Stage 171
4. Geological Structure 172
5. Correlations and Geological Age 174
6. Summary 176

1. Introduction.

The area under consideration is situated north-east of Attunga, a village on the Manilla Road, about thirteen miles north of Tamworth. It lies in the region of the Great Serpentine Belt, which is known to geologists by the researches of David and Pittman (1899) and W. N. Benson (1913–1918).

Outcrops of the limestones were mapped by L. J. Jones (1919) during the course of a State Survey of limestone deposits, but no detailed stratigraphical survey of the district has hitherto been attempted.

The present work is the result of an invitation of Mr. E. D. Coulter, Manager of Sulcor Quarry, four miles north of Attunga, to collect and examine large brachiopods (*Stringocephalus* sp., cf. *S. burtini* Defrance), which he had discovered in limestone north of the Quarry. As *S. burtini* is an important zone-fossil in the Middle Devonian of the Northern Hemisphere, it was considered desirable to ascertain the stratigraphical position of the *Stringocephalus* limestone in relation to the coral limestones of the Attunga and Tamworth districts. Consequently, all the limestone outcrops in the Parish of Burdekin and adjacent parishes have been examined and mapped, and collections have been made of fossils from all outcrops. On the basis of the field and laboratory study it has been found possible to work out the stratigraphical succession and some details of the geological structure in the Attunga district and to suggest correlations with formations in the Tamworth district and elsewhere.

The principal fossils collected are Rugose and Tabulate corals, stromatoporoids, Bryozoa, Brachiopoda and a few Mollusca. Many of these are species which were named and described from the Tamworth district by R. Etheridge, Junr. (1899) and W. S. Dun in Benson (1918); some are forms that previously were not known to occur in the Tamworth Province, but which had been found in the Devonian of the Murrumbidgee district and in other parts of eastern Australia; others again are species new to science.

The Rugose corals have been sectioned and sent for examination to Dr. Dorothy Hill of the University of Queensland; these have been described in a separate communication (Hill, 1942). It is hoped that the other groups will be similarly treated.

The writer is specially indebted to Mr. and Mrs. E. D. Coulter and family, of Attunga, for kindness and hospitality during the course of field work. The field-expenses of two visits to Attunga and Tamworth, in November, 1940, and February, 1942, were covered by a grant from the Commonwealth Research Fund administered by the University of Sydney.

2. Previous Investigation.

The sequence within the Tamworth Series south of Moore Creek was worked out by Benson (1913–1918) and summarised by him in 1922 and 1923. Benson followed Etheridge (1899) in regarding the series as of Middle Devonian age. He states: "They (the Tamworth Series) are an extensive series of radiolarian claystones with much tuff and three intercalated widely extending coral limestones" (1923, p. 26) . . . "the lowest (Nemingha) horizon is the most continuous, having been traced intermittently for over 150 miles. It is strongly brecciated and intimately associated with fragmental volcanic rocks of spilitic or keratophyric character. The intermediate Loomberah horizon has been traced for about 15 miles only, and seems to have been developed in an area where brief local emersion occurred exposing the newly-formed limestone to wave-action. The highest limestone (Moore Creek) has been recognised at intervals over a distance of 80 miles. Like the Nemingha Limestone, it shows no signs of emersion, but forms lenticular masses in the radiolarian claystone. There is, however, but little volcanic material with the two upper limestones . . . The maximum igneous activity occurred immediately following on the formation of the Nemingha limestones, and extensive masses of spilitic pillow-lava have been formed in the Nundle district, and it is also found on a horizon below the Nemingha limestone" (1922, pp. 97–98).

A columnar section of the series is given by Benson (1922, Pl. XIVa).

The limestones outcropping north of Moore Creek, usually known as the Attunga limestones, have been assumed by Benson (1918, p. 697) and by Carne and Jones (1919, pp. 254–256) to belong to the Moore Creek horizon, and the geological ranges of fossils quoted by Benson (1922) are based on this supposition. Nevertheless Benson wrote: "The presence of *Phillipsastræa*, *Tryplasma* sp. and *Favosites multitabulata* suggests that the Loomberah limestone may also be represented. If this be so, we may here have an opportunity of checking the present tentative assumption that the Loomberah limestone is stratigraphically intermediate between the Moore Creek and Nemingha limestones, though nearer to the former. It should be noted that, in one place at least, namely on the top of the hill behind the Burdekin Homestead, the limestone of the Moore Creek horizon is brecciated, and set in a red matrix, in a manner previously believed to be confined to the Nemingha limestone" (1918, p. 698). He also recognised that the limestone masses occur as "isolated portions of folds, compressed and faulted, the whole indicating an extremely complex tectonic structure" (1918, p. 697).

The present note is concerned chiefly with these Attunga limestones.

3. Stratigraphy.

(See Text-fig. 1.)

The road from Tamworth to Manilla, north of Moore Creek, follows approximately the geological boundary between the Upper Devonian sediments of the

Barraba Series to the west and the Lower and Middle Devonian sediments of the Tamworth Series to the east, the latter forming the foothills of the Moonbi Range, the south-western portion of the New England Plateau.

The Palæozoic rocks outcrop chiefly on the hills, and the intervening valleys are filled with thick alluvium and drift, parts of which date back to the Pleistocene. The latter contain remains of extinct marsupials, as in Catong Gully (Por. 34, Par. Bubbogullion), where Mr. Quick and Mr. E. D. Coulter have collected teeth and bones of *Diprotodon australis* Owen and *Macropus anak* Owen, *M. brehus* Owen and *Procoptodon thomsoni* Krefft, specimens of which are in the Australian Museum, Sydney. This cover of Post-Tertiary deposits contributes largely to the difficulty of interpreting the geological structures in the underlying rocks.

North of Moore Creek there outcrops a series of tuffs, (?) spilites, limestones and banded cherts, which appear to be equivalent to the complete sequence of the Tamworth Series occurring between Moore Creek and Nundle as described by Benson (1913-1918). The limestones of the Attunga district occur on three distinct horizons, and are lithologically and palæontologically similar to the Nemingha, (?) Loomberah and Moore Creek limestones, in the stratigraphical order assumed by Benson. It is proposed to divide the Tamworth Series into three, the Nemingha, Sulcor and Moore Creek Stages, named for the typical limestones developed respectively within each.

The order of succession of the beds in the Tamworth Series north of Moore Creek appears to be as follows (in descending order) :

Moore Creek Stage.
- Radiolarian Cherts.
- Limestone.

Sulcor Stage.
- Cherts and Tuffs.
- Limestone.

Nemingha Stage.
- Upper Cherts and Tuffs.
- Limestone.
- Lower Cherts and Tuffs.

The beds have been thrown into a series of gentle folds grouped to form a major synclinal structure, whose axis runs meridionally, with a gentle pitch to the north. The structure is further complicated by faulting, both parallel to and transverse to the main fold-axis. Subsequent erosion and deposition of alluvium have produced the isolated outcrops indicated on the map (Text-fig. 1).

(a) Nemingha Stage.

Lower Cherts and Tuffs. In the parish of Attunga, between Moore Creek and Attunga Creek, a sequence of banded tuffs and cherts forms the foothills of the Moonbi Range, but this has not been examined in detail. It is of considerable but unknown thickness ; the base is not exposed, as the rocks have been intruded by the Moonbi granite. Along Attunga Creek the upper parts of the sequence are exposed in a quarry on the north side of the creek, and in a cutting below the limestone near Burdekin Homestead. On the Manilla Road near the 15 mile-peg these tuffs dip in an easterly direction below the limestones of the Broken Hill Pty. Quarry.

Limestone. Limestones that are similar to those at " Beedle's Freehold ", Por. 167 south to Por. 163, Par. Nemingha, occur as a number of isolated outcrops in the parishes of Attunga and Burdekin. In the Parish of Attunga an outcrop occurs in Pors. 191–109 on the western side of Boundary Creek, a northern

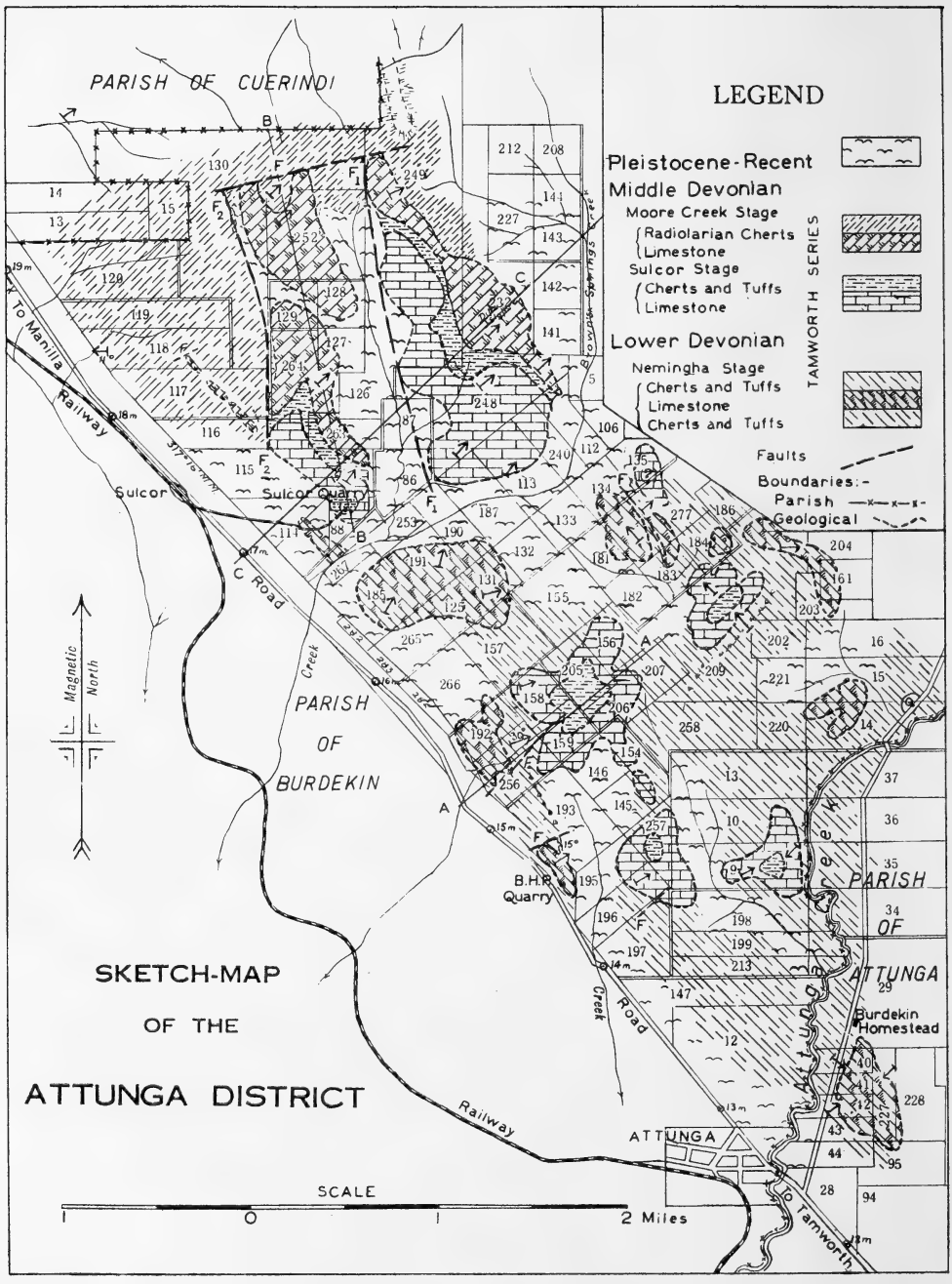

Fig. 1. Geological Sketch Map of the Attunga District.

tributary of Moore Creek. This is along the line of strike of the typical Moore Creek limestone, from which it must be separated by a fault along Moore Creek. It is probable that some of the fossils in old collections come from this limestone and are recorded as " Moore Creek " fossils. Other outcrops occur on the hill behind Burdekin Homestead in portions 40–43 and 228, and also in portion 159, Par. Attunga. This limestone is exposed in a number of places in the Parish of Burdekin, as shown on the accompanying map (Text-fig. 1), particularly in the hills immediately east of the Manilla Road.

The limestone is well-bedded in its lower portions, as in Por. 185, but the upper parts are more massive. It has been quarried in the Reserve near Pors. 193–195, Par. Burdekin by Broken Hill Proprietary, Limited.

The rock has suffered some regional metamorphism and is partly marmorised. In Portion 184 there is a red, crinoidal marble suitable for ornamental purposes. In some places the rock shows peculiar brecciation, whose origin is somewhat obscure ; in some places it is developed as a result of faulting, but in the main it seems to have been an original structure in the rock ; Benson has already noted its occurrence in the Nemingha Limestone in the Parishes of Nemingha and Loomberah. A good typical exposure occurs in the bed of the creek in Por. 256, where angular and rounded fragments of white, fossiliferous limestone are set in a matrix of pink sedimentary limestone. Such a rock might have been formed as a beach, or shallow-water deposit adjacent to a coral reef.

Fossils are fairly abundant on certain horizons, the common forms being stromatoporoids, Tabulate corals, crinoid stems and Bryozoa. Rugose corals are more rare, but are distinctive.

The following forms have been identified from outcrops in the Parishes of Burdekin and Attunga :

Acanthophyllum cf. *mansfieldense* (Dun)
Lyrielasma floriforme Hill.
Xystriphyllum insigne Hill.
" *Cystiphyllum* " *multitrabeculatum* Hill.
Spongophyllum halysitoides Eth. fil.
Tryplasma sp.
Syringopora spp.
Heliolites porosa Goldf.
Heliolites sp.
Favosites goldfussi d'Orb.
Favosites pittmani Eth. fil.
Litophyllum koninckı Eth. fil. and Foord.
(*?*) *Chætetes* sp.
(*?*) *Alveolites* sp.
Stromatoporoids.
Crinoid Stems.

From the type-locality in the Parish of Nemingha the following forms have been identified :

Spongophyllum halysitoides Eth. fil.
Favistella neminghensis (Eth. fil.).
Tryplasma sp.
Syringopora (*?*) *auloporoides* de Kon.
Syringopora porteri Eth. fil.
Favosites basaltica var. *moonbiensis* Eth. fil.
Favosites multitabulata Eth. fil.
Favosites pittmani Eth. fil.
Favosites goldfussi d'Orbigny.
? Favosites salebrosa Eth. fil.
? Thamnopora foliata Jones.

The relative abundance and variety of the Tabulate corals is worthy of further investigation.

Upper Cherts and Tuffs. Overlying the limestones of the Nemingha stage and apparently conformable with them are banded tuffs and cherts. These are well-bedded and fine-grained ; so far as is known they are unfossiliferous, except for a narrow band of limestone-breccia. This occurs about half-way up the sequence and is composed of white crystalline limestone fragments, from a few inches to three or four feet in diameter, usually consisting of broken colonies of *Favosites*, *Heliolites* and stromatoporoids, apparently derived from the under-

lying limestone, set in a dark-coloured matrix of tuffaceous material which weathers to a greenish colour. The occurrence suggests a storm-beach of limestone boulders on which showers of volcanic ash were deposited. This band is followed by a (?) flow of altered igneous rock, possibly spilitic in character.

A good section is exposed on the south-eastern slope of the hill in Portion 209, near Portion 202, Parish of Burdekin. The limestone-breccia here is similar to that occurring in Portions 167–168, Parish of Nemingha, and elsewhere in the Nemingha Stage.

At Willowtree Creek (Por. 54, Par. Gill), and The Horse Arm Creek (Por. 226, Par. Attunga) there are outcrops of Nemingha limestone and overlying tuff with interbedded limestone-breccia, as mentioned by Benson (1918, p. 695). The rocks in these places have suffered contact-metamorphism through the intrusion of the Moonbi granite, with the production of garnet, vesuvianite, wollastonite and other contact-minerals.

(b) Sulcor Stage.

Limestone. The Nemingha Stage is followed by limestones occurring in about six isolated outcrops in the Parish of Burdekin, as indicated on the map (Text-fig. 1). The limestone varies in thickness from about 50 feet to nearly 200 feet. Bedding is usually well-defined, owing to the surface silicification of the fossils in natural outcrops, although the rock as a whole carries little impurity; analyses show approximately 98 per cent. $CaCO_3$. The rock appears to be much less altered than limestones of the Nemingha Stage; local brecciation occurs in the vicinity of small faults.

The limestone, which may be called the Sulcor Limestone, is quarried in Portions 88–115, Parish of Burdekin, by Sulphide Corporation, Limited.

Parts of the limestone are very fossiliferous, and an interesting collection has been made of new forms and of forms not hitherto known to occur in the Tamworth district, which permit correlation of this limestone with formations in other parts of New South Wales.

The best collecting-ground for fossils is at the back of the quarry, in Portion 88 and in the eastern end of Portion 115. Here detailed zoning of the beds is possible, and more new forms may be revealed. Similar fossils have been collected in the upper part of the creek bed in Portion 248 and from other outcrops indicated on the map as belonging to this Stage, but the variety is not so great.

The following forms have been obtained from the Sulcor limestone and are in the collections of the University of Sydney:

Receptaculites australis Salter.
Xystriphyllum magnum Hill.
Xystriphyllum mitchelli (Eth. fil).
Prismatophyllum browncæ Hill.
Trapezophyllum coulteri Hill.
Phillipsastræa maculosa Hill.
Phillipsastræa linearis Hill.
Phillipsastræa carinata Hill.
Eridophyllum bartrumi Allan.
Mictophyllum cf. *creswelli* (Chapman).
Pseudamplexus princeps (Eth. fil).
Aulacophyllum trizonatum Hill.
Syringopora speleana Eth. fil.
Syringopora spp.
Favosites spp. (massive and dendroid).
Litophyllum sp.
Heliolites spp.
Plasmopora sp.
Stromatoporoids.
Stromatoporella loomberensis Dun.
Strophomenid.
Pentamerid.
Atrypa sp.
Large gastropod.

The following forms were obtained in Por. 23, Par. Loomberah, from the Loomberah limestone, which is here correlated with the Sulcor limestone.

Eddastræa grandis (Dun).
Phillipsastræa aperta Hill.
Phillipsastræa callosa Hill.
Endophyllum cf. *abditum* Edwards and Haime.
Favosites sp.
Heliolites sp.
(*?*) *Litophyllum* sp.
Stromatoporella loomberensis Dun.
Stromatoporella bensoni Dun.
(*?*) *Chætetes stelliformis* Chapman.
Batostomella sp.

Banded Cherts and Tuffs. The limestones of the Sulcor Stage are succeeded by banded cherts and tuffs which outcrop in Portions 115–263, Portions 248–249, and on the tops of hills in Portions 158–159–205, 209, 257, and in Portion 9.

The rocks are fine-grained and make rather poor outcrops. They contain traces of small brachiopods, and are probably of marine origin.

(c) The Moore Creek Stage.

Limestones. In the Parish of Burdekin this Stage has its best development along the limestone ridge north of Sulcor Quarry, from the eastern end of Por. 115 to " Follington's Limestone " in Portion 252.

The limestones are well-bedded, and are possibly of the order of 400 feet in thickness. No trace of interbedded shaly material has been observed. Certain bands in the limestones have suffered differential chemical weathering, producing shallow trenches, which have become filled with *terra rossa* and wash from the adjacent sediments. One such apparent break in the succession occurs in Portion 128–129, marking a division into a lower and an upper portion which contain distinct faunas.

The limestones have a general dip to the north-east at angles of 15 degrees or less, and much of the outcrop shown on the map is on a dip-slope. To the east the limestones plunge under the alluvium and drift of the valley-floor and to the west they are truncated by a meridional fault which has thrown them against radiolarian cherts of a stratigraphically higher horizon. The faulting has caused a drag on the limestones, producing a small anticlinal structure.

The small isolated outcrops of limestone in Portions 117–118 are thin cappings whose presence is probably due to faulting, but the field-evidence is insufficient for an adequate explanation of their occurrence. The most northerly outcrop contains fossils of the upper part of the Moore Creek limestone.

The sequence of the Moore Creek limestones is repeated along the crest of the ridge to the east, running from the north-east corner of Portion 248 through Portion 232 and diagonally through the central part of Portion 249. Again the limestones dip to the north-east and much of the outcrop is on a dip-slope which plunges below the alluvial deposits of the valley to the east.

The lowest bed of limestone forms bluffs ten to twenty feet in height around the " amphitheatre " in Por. 264, and along the south-western crest of the hill in Por. 232, 249. This is succeeded by bedded limestone with very abundant *Amphipora* spp. Near the eastern end of the boundary between Portions 115 and 263 there is an abundance of the large brachiopod *Stringocephalus* cf. *burtini* Defrance. This form occurs also in abundance at the top of the hill in the south-west corner of Por. 232.

The overlying limestone bed in Por. 264 contains *Sanidophyllum colligatum* (Eth. fil), " *Cystiphyllum* " sp., *Stringophyllum* spp., *Mesophyllum* sp., *Syringopora* sp., *Favosites* sp., *Heliolites* sp., *Amphipora* and Stromatoporoids.

The upper part of the limestone, forming the hill in Portion 252 (Follington's), contains all the species that are found in the limestone occurring at the well-known locality south of Moore Creek, in Portions 61, 140, and R1472s in the Parish of Woolomol and along the west of Spring Creek in Tamworth

Common, about a mile north of Tamworth. This limestone also dips gently to the north-east and is fossiliferous throughout.

The following fossils have been collected from the limestones of the Moore Creek Stage in the Parishes of Burdekin and Woolomol :

Sponges, undetermined.
Dohmophyllum sp.
Xystriphyllum mitchelli (Eth. fil).
" *Campophyllum* " cf. *lindstromi* (Frech.).
" *Cystiphyllum* " *australe* Eth. fil.
Mesophyllum cornubovis (Eth. fil).
Disphyllum cf. *gregorii* (Eth. fil).
Disphyllum robustum (Eth. fil).
Phacellophyllum porteri (Eth. fil).
Sanidophyllum davidis Eth. fil.
Sanidophyllum colligatum (Eth. fil).
Favistella cf. *rhenana* (Frech).
(*?*) *Tryplasma* sp.
Spongophyllum giganteum Eth. fil.
Spongophyllum ? immersum Hill.
Stringophyllum bipartitum Hill.
Stringophyllum densum Hill.
Microplasma parallelum Eth. fil.
Syringopora auloporoides Eth. fil.
Syringopora porteri Eth. fil.
Favosites goldfussi d'Orb.
Favosites salebrosa Eth. fil.
Emmonsia squamulifera (Eth. fil).
? Striatopora crummeri (Eth. fil).
Heliolites porosa Goldf.
Litophyllum konincki Eth. fil.
Amphipora sp.
Fenestella mouara Crockford.
Crinoid Stems.
Stringocephalus cf. *burtini* Defrance.
Atrypa spp.

Radiolarian Cherts. At the north end of Por. 252 (Follington's) the *Sanidophyllum* limestone passes into a sandy bed which is overlain by Radiolarian cherts, similar in all respects to those occurring in the Council Quarry in Tamworth Common. The Tamworth cherts yielded the rich radiolarian fauna described by Hinde (1899).

These rocks are fine-grained banded tuffs, black when fresh, weathering to black and white bands.

They also outcrop in the northern end of Por. 248, and in the hills in Portions 117–119, and supply quantities of angular boulders distributed over the surface of alluvial deposits covering all the low ground in the neighbourhood.

4. Geological Structure.

A striking feature of the limestones in the vicinity of Sulcor Quarry is their uniform dip to the north-east ; south of Moore Creek the dips in the Tamworth Series are to the south-west.

In the southern part of the Parish of Burdekin the limestones are very gently folded, and near the Yarramanbully Road, north of Attunga Creek, they dip to the west, thus indicating that the major structure is a syncline, pitching to the north and having its axis along the upper valley of Brown's Springs Creek (Text-fig. 2, C–C).

The structure is somewhat complicated by the occurrence of two faults, approximately parallel to this axis. The first fault F_1–F_1 (on map, Text-fig. 1) running through Portions 247 and 248 causes the repetition of the Sulcor and Moore Creek limestones in two parallel hills. The throw of this fault must be of the order of 500 feet, as shown in Text-fig. 2, C–C. The other fault, F_2–F_2, runs approximately along the eastern boundary of Por. 120 and throws Radiolarian Chert against limestones of a lower horizon, but, in the absence of a datum-horizon, the amount of its throw cannot be measured.

A series of faults of less magnitude occurs approximately at right angles to the synclinal axis ; apparently one such fault truncates the limestones at the north end of Follington's and in Por. 249, where the bedding of the limestones ends abruptly against Radiolarian Cherts.

Several other small cross-faults are found amongst the limestones close to the Manilla-Tamworth Road, as shown on the map.

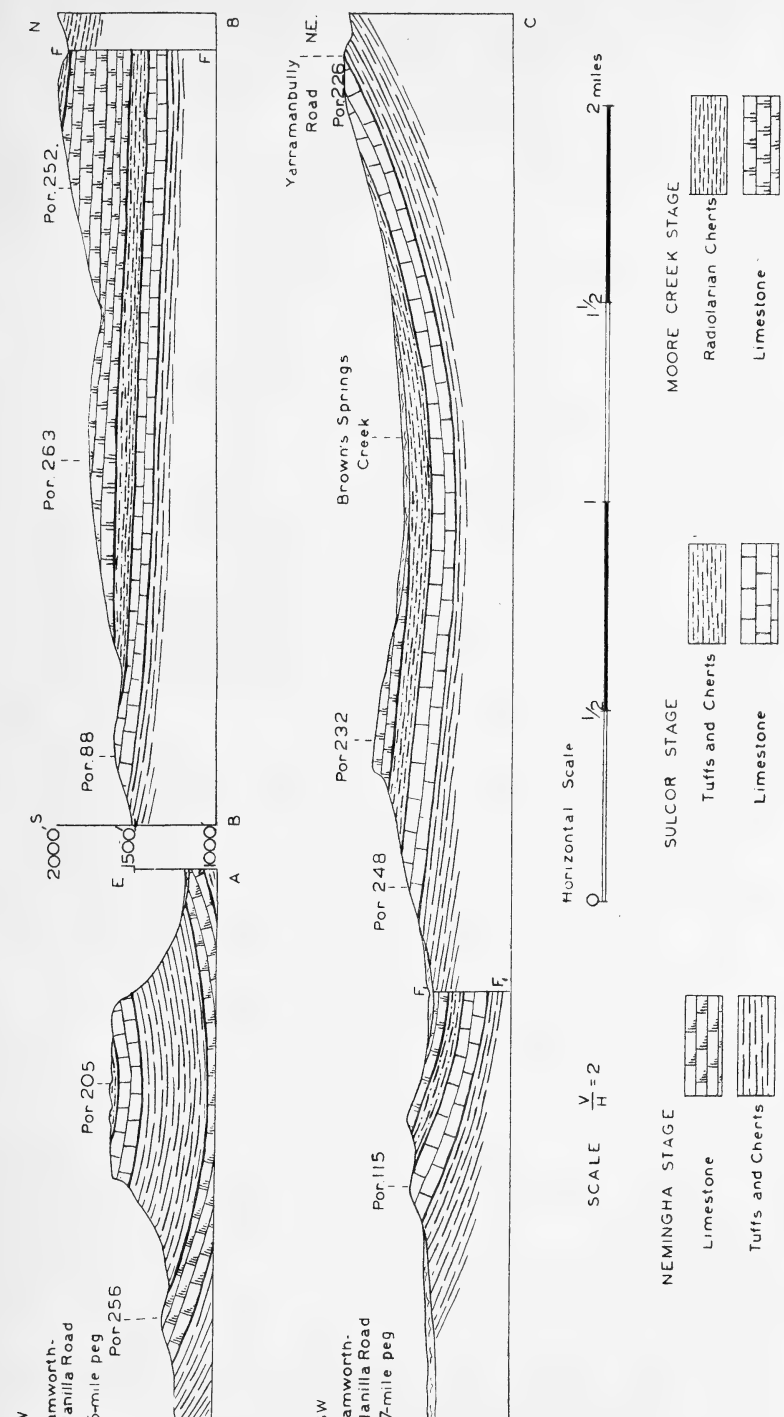

Fig. 2. Generalized Sections through the Tamworth Series, Parish of Burdekin.

With regard to the structural relations of the Tamworth Series to younger formations, the field-evidence north of Attunga strongly suggests an angular unconformity between it (the Tamworth Series) and the Upper Devonian Barraba Series, outcropping to the west, with westerly dips. Farther north, however, the evidence is not so clear, so that the structural relations require further investigation.

5. Correlations and Geological Age.

The field-work leaves no doubt of the order of succession of the limestones and the associated sediments in the area under consideration. A section from about the 15-mile peg on the Oxley Highway in a north-easterly direction (Text-fig. 2, A–A) shows the Nemingha Stage, including limestone, with *Xystriphyllum insigne*, overlain by limestone containing Sulcor fossils. An oblique section along the ridge north of Sulcor Quarry shows Sulcor limestone, tuffs and cherts overlain by the Moore Creek Stage (Text-fig. 2, B–B).

Comparing this order of succession with that of the Tamworth Series south of Moore Creek, we find that the lowest division in both areas consists of the products of igneous activity interbedded with slightly metamorphosed limestones, showing similar lithological and faunal characteristics. This sequence is here called the Nemingha Stage.

The limestone of the Sulcor Stage at Attunga and the Loomberah Limestone of the type area show general similarities and are probably of about the same age; they both contain rather abundant *Phillipsastræa*, a genus which is not known from any other limestones of the district. The outcrops of the Loomberah limestone are very limited in extent.

The limestones near the top of the Tamworth Series in the Parishes of Burdekin and of Woolomol are similar lithologically and contain identical species. There can be no doubt that these are both parts of the Moore Creek Stage.

The present work has therefore confirmed Benson's assumption of the stratigraphical order of the limestones of the Tamworth Series.

General comparisons with other Devonian formations in New South Wales can be made, but exact correlations are hampered by lack of detailed field-work in the areas concerned.

In the Murrumbidgee district, 15 miles south of Yass, a series of tuffs and lavas, the Black Range Series, unconformably overlies the Silurian rocks of the Yass district. Shearsby (1905) correlated these with the Lower Devonian "Snowy River Porphyries" of eastern Victoria. This igneous series is overlain by limestones of the Murrumbidgee Series, which are richly fossiliferous. The Rugosa are described by Hill (1940). As a result of reconnaissance work the writer is of the opinion that they are not nearly so thick as suggested by Harper (1909), but that they are thrown into a series of folds, causing repetition of the various limestone bands. Fossils have been collected rather indiscriminately from various horizons, causing confusion in the faunal sequence and correlations, which will vanish with detailed field-mapping and systematic collecting. Collections made over the past few years have increased the number of known species and have decreased the differences supposed by Benson (1922) to exist between the faunas of the Murrumbidgee and Tamworth provinces, but the correlations are mainly with the limestone of the Sulcor Stage, and not with the overlying Moore Creek Stage.

Several important forms are common to the Murrumbidgee and Sulcor limestones. These include *Receptaculites australis*, *Xystriphyllum mitchelli*, *Eridophyllum bartrumi*, *Pseudamplexus princeps*, *Syringopora speleana* and species of *Favosites*.

From the Molong district Devonian rocks have been described by Dr. Germaine Joplin and Miss Alma Culey (1938). Between Silurian and Upper Devonian sediments there lies a series named by them the Garra Beds. These consist of cherts and tuffs at the base, with overlying " limestones, calcareous shales and fissile clay-slates ", which are fossiliferous. The limestones occur in isolated outcrops and the detailed order of succession within the sequence has not yet been worked out. The relative abundance of *Receptaculites australis*, *Pseudamplexus princeps* and a few other forms led to the correlation of the Garra Beds with those of the Murrumbidgee. Subsequent work on the corals by Hill and Jones (1940) proved the presence also of forms indicating an age greater than that of the known Murrumbidgee fossils, but it is the writer's opinion that the Garra Beds represent a considerable time-interval and are probably equivalent to both the Nemingha and Sulcor Stages of the Tamworth Series.

Since the Garra Beds are followed directly by Upper Devonian sediments, the equivalent of the Moore Creek Stage is missing, and there would appear to be a non-sequence in the succession.

In the Wellington district of New South Wales, north of Molong, Miss Basnett and Miss Colditz have found limestones from which Dr. Hill has identified Rugosa (1942), some of which are identical with species in the Loomberah limestone. Further information on this district will be published soon.

Other occurrences of Middle Devonian rocks in New South Wales which contain *Receptaculites australis* are known at Capertee and Tarago ; these are tentatively correlated with similar beds in the Murrumbidgee Series.

Dr. Hill's work on the Rugosa of the Tamworth district (1942) and her correlations with forms in other States and in Europe are valuable contributions to our knowledge of Devonian stratigraphy.

She has deduced, from a study of the Rugosa, that

(1) the Nemingha (*insigne*) fauna is Lower Devonian or possibly early Couvinian,
(2) the Loomberah (*Eddastræa*) and Sulcor (*Eridophyllum*) faunas are possibly both early Couvinian, not necessarily on the same horizon, and
(3) the Moore Creek (*Sanidophyllum*) fauna is Givetian in age.

The last correlation is confirmed by the presence of *Stringocephalus* cf. *burtini*, which is an important form in the lower part of the Givetian of the Paffrath Basin.

The relative ages of some of the New South Wales Lower and Middle Devonian rocks and their probable European equivalents are indicated in the following table :

Age.	European Stages.	Tamworth.	Murrumbidgee.	Molong.
Upper Devonian.	Famennian Frasnian.	Barraba Series.	—— ——	Lambie Stage. ——
Middle Devonian.	Givetian. Couvinian.	Moore Crk. Stage. Sulcor Stage.	—— Murrumbidgee Series.	—— Garra Beds.
Lower Devonian.	Coblenzian. Gedinnian.	Nemingha Stage. Tuffs, etc.	Black Range Series.	Garra Beds.

An interesting deduction from these correlations concerns the age of the Woolomin Series of cherts and jaspers occurring to the east of the Tamworth Series and mainly on the opposite (eastern) side of the Great Serpentine intrusions. This series was formerly regarded as probably Lower Devonian, but it would now seem that it is pre-Devonian in age.

6. Summary.

The paper describes the structure and stratigraphy of the Tamworth Series near Attunga, N.S.W.

The series is divided into three stages, named the Nemingha, Sulcor and Moore Creek Stages respectively, each including limestone with a reef-coral fauna. The first contains fossils which are Lower Devonian in age, the others are probably Middle Devonian, the (upper) Moore Creek Stage being equivalent to the Givetian of the European succession.

The sequence is correlated with other formations in New South Wales, and the paper is accompanied by a geological map and sections.

Bibliography.

Benson, W. N., 1913. The Geology and Petrology of the Great Serpentine Belt of New South Wales. Part I. Introduction. *Proc. Linn. Soc. N.S.W.*, **38**, (3), 491.

———— 1914. *Ibid.* Part II. The Geology of the Nundle District. *Proc. Linn. Soc. N.S.W.*, **38** (for 1913), (4), 569.

———— 1915. *Ibid.* Part V. The Geology of the Tamworth District. *Proc. Linn. Soc. N.S.W.*, **40**, (3), 540.

———— 1918*a*. *Ibid.* Part VI. Appendix. The Attunga District. *Proc. Linn. Soc. N.S.W.*, **42** (for 1917), (4), 693.

———— 1918*b*. *Ibid.* Part VII. The Geology of the Loomberah District and a Portion of the Goonoo Goonoo Estate. *Proc. Linn. Soc. N.S.W.*, **43**, (2), 320.

———— 1922. Materials for the Study of the Devonian Palæontology of Australia. *Rec. geol. Surv. N.S.W.*, **10**, (II), 83.

———— 1923. Palæozoic and Mesozoic Seas in Australasia. *Trans. N.Z. Institute*, **54**, 1.

Carne, J. E., and Jones, L. J., 1919. The Limestone Deposits of New South Wales. *Mineral Resources, No.* 25, *geol. Surv. N.S.W.*

David, T. W. E., and Pittman, E. F., 1899. On the Palæozoic Radiolarian Rocks of New South Wales. *Quart. J. geol. Soc. Lond.*, **55**, 16.

Dun, W. S., 1918. In Benson, W. N., 1918*b*.

Etheridge, R., Junr., 1899. On the Corals of the Tamworth District, chiefly from the Moore Creek and Woolomol Limestones. *Rec. geol. Surv. N.S.W.*, **6**, (3), 151.

Harper, L. F., 1909. The Geology of the Murrumbidgee District, near Yass. *Rec. geol. Surv. N.S.W.*, **9**, (I), 1.

Hill, Dorothy, 1941. The Lower Middle Devonian Rugose Corals of the Murrumbidgee and Goodradigbee Rivers, N.S.W. *J. Roy. Soc. N.S.W.*, **74** (for 1940), (III), 247.

———— 1942. The Devonian Rugose Corals of the Tamworth District, N.S.W. *J. Roy. Soc. N.S.W.*, **76**, 142-164, pls. II-IV.

Hill, Dorothy, and Jones, O. A., 1940. The Corals of the Garra Beds, Molong District, N.S.W. *J. Roy. Soc. N.S.W.*, **74**, (II), 175.

Hinde, G. J., 1899. On the Radiolaria in the Devonian Rocks of New South Wales. *Quart. J. geol. Soc. Lond.*, **55**, 38.

Joplin, Germaine A., and Culey, Alma G., 1938. The Geological Structure and Stratigraphy of the Molong-Manildra District. *J. Roy. Soc. N.S.W.*, **71** (for 1937), (II), 267.

Shearsby, A. J., 1905. On the Occurrence of a Bed of Fossiliferous Tuff and Lavas between the Silurian and Middle Devonian at Cavan, Yass. *Proc. Linn. Soc. N.S.W.*, **30**, (2), 276.

ON CONTACT TRANSFORMATIONS ASSOCIATED WITH THE SYMPLECTIC GROUP.

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Communicated by PROFESSOR H. S. CARSLAW.

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1. In this note I shall give a new proof for a slight generalisation of the following well-known theorem of Frobenius (1879).

A linear transformation

$$(1) \qquad \begin{cases} y = Ax + Bp \\ q = Cx + Dp \end{cases}, \quad x = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}, \quad p = \begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_n \end{pmatrix}$$

in the $2n$ independent variables x_ν, p_ν which leaves invariant the skew-symmetric bilinear form

$$x'\bar{p} - x'p = \sum_{\nu=1}^{n} (x_\nu \bar{p}_\nu - \bar{x}_\nu p_\nu)$$

in the $4n$ variables x_ν, p_ν, $\bar{x}_\nu$, $\bar{p}_\nu$, has its determinant

$$(2) \qquad \delta = \begin{vmatrix} A & B \\ C & D \end{vmatrix} = +1.^1$$

There is no difficulty in proving that $\delta^2 = 1$. In order to prove the more precise statement (2), which is important in the theory of canonical transformations, formerly a representation of the determinant of a skew-symmetric matrix by means of the so-called Pfaffian aggregates was used, and also later proofs of the theorem[2] are not all as simple as may be desired. The proof given recently by Radon (1939) is based on a certain general lemma concerning the rank of matrices, proved by making use of continuity. In his paper Radon suggests that a proof avoiding these considerations may be found; apart from a minor addition this will be done here (§5). Thus the lemma which may be useful in other parts of matrix calculus appears in its most general form as to the algebraic domain over which it is valid.

The (unimportant) generalisation of the abovementioned theorem which may be justified by the short consideration in §§2 and 3 was suggested to me by a paper of A. Wintner (1934) where the whole matter is discussed from a different point of view. As to the proof, we begin with some particular cases (§4) to which we reduce the most general case by means of Radon's lemma (§6).

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[1] The usual notations of matrix calculus are employed here. Capitals A, B . . . are n-rowed square matrices, E is the unit matrix, A' the transpose of A. Small Latin letters x, p . . . without indices are columns, x', p' . . . the corresponding rows.

[2] Cf. Caratheodory (1935), Radon (1939), Siegel (1939), Weyl (1939), Williamson (1939). The name "symplectic group" has been introduced by Weyl instead of the formerly used "complex group".

2. We consider the transformation in $2n+1$ variables x_ν, p_ν, x_0, which arises from a linear transformation of the form (1) if we add the equation

$$y_0 = h(x,\ p) + h_0 x_0 \tag{3}$$

and only require that the transformation represented by (1) and (3) is a contact transformation in x, p, x_0:

$$q'dy - dy_0 = \varrho(p'dx - dx_0). \tag{4}$$

From here it follows that the function $h(x, p)$ has to be a quadratic form in the $2n$ variables x_ν, p_ν:

$$h(x,\ p) = x'H_1 x + 2x'Hp + p'H_2 p = (x',\ p')\begin{pmatrix} H_1 & H \\ H' & H_2 \end{pmatrix}\begin{pmatrix} x \\ p \end{pmatrix} \tag{5}$$

where H_1, H_2, H are square matrices with n rows, H_1, H_2 symmetric.[3] Further we find from (3) and (4)

$$\varrho = h_0 = \text{const.}$$

Putting the expressions (1) and (3) in (4), we get the relations

$$\begin{aligned} (A'C - 2H_1)x + (A'D - 2H - h_0 E)p &= 0 \\ (B'C - 2H')x + (B'D - 2H_2)p &= 0 \end{aligned}$$

whence we have

$$\begin{cases} 2H_1 = A'C = C'A \\ 2H_2 = B'D = D'B \qquad (H_1,\ H_2 \text{ symmetric !}) \\ 2H = C'B = A'D - h_0 E \end{cases} \tag{6}$$

$$A'D - C'B = h_0 E,\ D'A - B'C = h_0 E. \tag{7}$$

If, on the other side, we state the fact that (1) is a symplectic transformation, i.e.

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}' \begin{pmatrix} O & -E \\ E & O \end{pmatrix} \begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} O & -E \\ E & O \end{pmatrix},$$

we get easily the same relations between the matrices A, B, C, D with the only restriction $h_0 = 1$.[4]

3. By means of the relations (7) we can invert the transformation (1) if and only if $h_0 \neq 0$; we get

$$\begin{cases} x = \dfrac{1}{h_0} D'y - \dfrac{1}{h_0} B'q \\ p = -\dfrac{1}{h_0} C'y + \dfrac{1}{h_0} A'q. \end{cases} \tag{8}$$

Further we have, from (3) and (8),

$$\begin{aligned} x_0 &= -\frac{1}{h_0} h(x,\ p) + \frac{1}{h_0} y_0 = k(y,\ q) + \frac{1}{h_0} y_0 \\ &= y'K_1 y + 2y'Kq + q'K_2 q + k_0 y_0. \end{aligned} \tag{9}$$

[3] Not every quadratic form $h(x, p)$ comes into question here. In another paper to be published elsewhere I have established necessary and sufficient conditions for these forms. From here a new parametrization of the symplectic group is derived such that there are no exceptional elements (cf. H. Weyl (1939)).

[4] According to a remark due to Herglotz (1932) the matrix equations (6) and (10) can be interpreted as the so-called "reciprocal theorems" for linear dynamical systems, which are involved in the "bracket conditions" of Poisson and those of Lagrange respectively. Cf. Whittaker (1927).

The equations (8), (9) representing also a contact transformation, the relations (6), (7) between the matrices

$$A,\ B,\ C,\ D,\ H_1,\ H_2,\ H$$

will continue to be true if we replace them respectively by

$$\frac{D'}{h_0},\ -\frac{B'}{h_0},\ -\frac{C'}{h_0},\ \frac{A'}{h_0},\ K_1,\ K_2,\ K \quad \left[k_0 = \frac{1}{h_0}\right].$$

This leads immediately to the following set of relations, evidently equivalent to (6), (7)

$$\text{(10)} \qquad \begin{cases} -2h_0^2K_1 = DC' = CD' \\ -2h_0^2K_2 = BA' = AB' \\ 2h_0^2K = CB' = DA' - h_0E \end{cases}$$

$$\text{(11)} \qquad DA' - CB' = h_0E,\ AD' - BC' = h_0E.$$

By the relations (6) or (10) the matrix $\begin{pmatrix} A & B \\ C & D \end{pmatrix}$ is characterised as a Hamiltonian matrix (cf. Wintner, 1934).

4. We shall now calculate the determinant δ of this matrix. From (8) we know that $\delta \neq 0$ if $h_0 \neq 0$. First we suppose $|\ A\ | \neq 0$. Then it is possible to determine two matrices P, Q with n rows which satisfy the equation

$$\text{(12)} \qquad \begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} E & O \\ P & Q \end{pmatrix} \begin{pmatrix} A & B \\ O & E \end{pmatrix};$$

indeed this equation means

$$C = PA \text{ and } D = PB + Q$$

whence

$$\text{(13)} \qquad P = CA^{-1},\ Q = D - CA^{-1}B.$$

Thus by (12) we have

$$\text{(14)} \qquad \delta = \begin{vmatrix} A & B \\ C & D \end{vmatrix} = |\ Q\ |\ |\ A\ |.$$

In virtue of (10) and (11) we have

$$QA' = DA' - CA^{-1}BA' = DA' - CA^{-1}AB' = DA' - CB' = h_0E$$

and thus

$$\delta = |\ Q\ |\ |\ A\ | = |\ Q\ |\ |\ A'\ | = |\ QA'\ | = h_0{}^n.$$

For $h_0 = 1$ this is the theorem stated in §1.

In the same way we can prove the theorem if $|\ B\ | \neq 0$. Then it is possible to find two matrices U, V which satisfy the equation

$$\text{(15)} \qquad \begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} E & O \\ U & V \end{pmatrix} \begin{pmatrix} A & B \\ E & O \end{pmatrix} = \begin{pmatrix} A & B \\ UA + V & UB \end{pmatrix}$$

whence

$$\text{(16)} \qquad U = DB^{-1},\ V = C - DB^{-1}A.$$

By (10) we have

$$VB' = CB' - DB^{-1}AB' = CB' - DA' = -h_0E;$$

hence

$$\text{(17)} \qquad \delta = (-1)^n|\ V\ |\ |\ B\ | = (-1)^n\ |\ -h_0E\ | = h_0{}^n.$$

5. Generally we cannot suppose $|A| \neq 0$ or $|B| \neq 0$. We can only suppose that the $n \times 2n$ — matrices (A, B) and (C, D) have the rank n, because otherwise the matrix $\begin{pmatrix} A & B \\ C & D \end{pmatrix}$ could not be regular. To establish the theorem also in this case we shall generalise the product formula (12) or (15) by means of the following lemma of Radon, which we shall prove here algebraically:

LEMMA: *If the $n \times 2n$ — matrix (A, B) with elements in the infinite integral domain Δ has the rank $r \leqslant n$, then there is a diagonal matrix*

$$S = \begin{pmatrix} s_1 & & & O \\ & s_2 & & \\ & & \ddots & \\ O & & & s_n \end{pmatrix} \quad \text{with } s_\nu \text{ in } \Delta,$$

such that the matrix $AS + B$ has the rank r.[5]

Proof: First we shall suppose $r = n$ (the only case we need actually here). Let $A = (a^{(1)}, a^{(2)}, \ldots, a^{(n)})$, $B = (b^{(1)}, b^{(2)}, \ldots, b^{(n)})$ where $a^{(\nu)}, b^{(\nu)}$ are the columns of A and B. If S is a diagonal matrix with indeterminate diagonal elements s_ν, we have

$$AS + B = (s_1 a^{(1)} + b^{(1)}, s_2 a^{(2)} + b^{(2)}, \ldots, s_n a^{(n)} + b^{(n)})$$

and hence the determinant

$$\begin{aligned} |AS + B| = s_1 s_2 \ldots s_n \, |a^{(1)}, a^{(2)}, \ldots, a^{(n)}| + \sum_{\nu=1}^{n} s_1 \ldots s_{\nu-1} s_{\nu+1} \ldots s_n \times \\ \times |a^{(1)}, \ldots, a^{(\nu-1)}, b^{(\nu)}, a^{(\nu+1)}, \ldots, a^{(n)}| + \ldots \\ + \sum_{\nu=1}^{n} s_\nu \, |b^{(1)}, \ldots, b^{(\nu-1)}, a^{(\nu)}, b^{(\nu+1)}, \ldots, b^{(n)}| \\ + |b^{(1)}, b^{(2)}, \ldots, b^{(n)}|. \end{aligned}$$

This polynomial in the n indeterminates $s_1, s_2, \ldots, s_n$ over Δ cannot be identically zero because at least one of its coefficients is different from zero; since there are in (A, B) exactly n linearly independent columns, say $a^{(\nu_1)}, a^{(\nu_2)}, \ldots a^{(\nu_k)}, b^{(\nu_{k+1})}, \ldots b^{(\nu_n)}$, the coefficient of $s_{\nu_1} s_{\nu_2} \ldots s_{\nu_k}$ will be different from zero. Therefore one can choose values of $s_1, s_2, \ldots s_n$ in Δ such that the square matrix $AS + B$ has the rank n.

If $r < n$ we shall apply the same procedure. Let $a^{(\mu_1)}, \ldots, a^{(\mu_k)}, b^{(\mu_{k+1})}, \ldots b^{(\mu_r)}$ be a set of r linearly independent columns of (A, B). Then a certain square submatrix $(\bar{A}, \bar{B})$ formed by r rows of the matrix $(a^{(\mu_1)}, \ldots, a^{(\mu_k)}, b^{(\mu_{k+1})}, \ldots, b^{(\mu_r)})$ has the rank r. Let

$$(\bar{A}, \bar{B}) = (\bar{a}^{(\mu_1)}, \ldots, \bar{a}^{(\mu_k)}, \bar{b}^{(\mu_{k+1})}, \ldots, \bar{b}^{(\mu_r)})$$

where the columns $\bar{a}^{(\mu_\varkappa)}, \bar{b}^{(\mu_\varrho)}$ arise from $a^{(\mu_\varkappa)}, b^{(\mu_\varrho)}$ by omitting certain $n - r$ elements, all in the same rows of (A, B). Then as above we see that the submatrix

$$(s_{\mu_1} \bar{a}^{(\mu_1)} + \bar{b}^{(\mu_1)}, \ldots, s_{\mu_k} \bar{a}^{(\mu_k)} + \bar{b}^{(\mu_k)}, s_{\mu_{k+1}} \bar{a}^{(\mu_{k+1})} + \bar{b}^{(\mu_{k+1})}, \ldots, s_{\mu_r} \bar{a}^{(\mu_r)} + \bar{b}^{(\mu_r)})$$

of $AS + B$ with r rows and r columns has "generally" the rank r; for its deter-

[5] Radon (1939) only stated the existence of a *symmetric* matrix S with this property, and only if Δ is the field of all real or complex numbers. In the paper mentioned in note (3) I have proved that if (A, B) is of rank n, one can impose on S the condition $SB = B'S$, i.e. SB to be symmetric.

minant is a certain polynomial in $s_{\mu_1}, s_{\mu_1}, \ldots, s_{\mu_r}$, which has not all its coefficients equal to zero. At least we have $| a^{(\mu_1)}, \ldots, a^{(\mu_k)}, b^{(\mu_{k+1})}, \ldots, b^{(\mu_r)} | \neq 0$; this is the coefficient of $s_{\mu_1}, s_{\mu_2} \ldots s_{\mu_k}$.

The following generalisation of Radon's lemma which easily follows from our proof may be stated here. *Let A_λ, B_λ ($\lambda = 1, 2, \ldots, l$) be l pairs of square matrices over Δ such that the $n \times 2n$ — matrices (A_λ, B_λ) have the ranks $r_\lambda \leqslant n$. Then o n e diagonal matrix S over Δ can be found for which the l matrices $A_\lambda S + B_\lambda$ have the ranks r_λ (resp.).*

6. According to the lemma we determine a diagonal matrix S for which $AS + B$ has the rank n. Then to the matrix

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} E & S \\ O & E \end{pmatrix} = \begin{pmatrix} A & AS + B \\ C & CS + D \end{pmatrix} = \begin{pmatrix} A & B^* \\ C & D^* \end{pmatrix},$$

which has the same determinant as the matrix $\begin{pmatrix} A & B \\ C & D \end{pmatrix}$ we can apply the formula (15) with B^*, D^* instead of B, D. By (16) we have

$$V^* = C - D^*B^{*-1}A = C - (CS + D)(AS + B)^{-1}A$$

and

$$V^*B^{*\prime} = CSA' - CB' - (CS + D)(AS + B)^{-1}(ASA' + AB').$$

Now we make use of the conditions (10); thus we get

$$\begin{aligned} V^*B^{*\prime} &= CSA' - CB' - (CS + D)(AS + B)^{-1}\ (AS + B)A' \\ &= CSA' - CB' - CSA' - DA' = -h_0E \end{aligned}$$

whence (17) gives again $\delta = {h_0}^n$.

References.

Caratheodory, C., 1935. *Variationsrechnung und partielle Differentialgleichungen erster Ordnung*, Teubner, Leipzig, §§95, 96, 102.

Frobenius, G., 1879. *Crelle's J. f. Math.*, **86**, 44.

Herglotz, G., 1932. Geometrische Optik, Lectures, Göttingen, unpublished.

Radon, J., 1939. *Monatsh. f. Math.*, **48**, 198.

Siegel, C. L., 1939. *Math. Ann.*, **116**, 617.

Weyl, H., 1939. The Classical Groups, Princeton, pp. 166-167.

Whittaker, E. T., 1927. Analytical Dynamics of Particles and Rigid Bodies. Cambridge, Chap. XI.

Williamson, J., 1939. *Bull. Amer. Math. Soc.*, **45**, 307.

Wintner, A., 1934. *Annali di Mat.*, (IV), **13**, 105.

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MIDDLE PALÆOZOIC RUGOSE CORALS FROM THE WELLINGTON DISTRICT, N.S.W.

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With Plates V and VI.

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Lists of Rugose coral species from various localities near Wellington are given, and it is deduced from them that at least three distinct faunas are present: (1) a *Halysites* fauna of Silurian or at latest Gedinnian age; (2) a Garra fauna, probably of Coblenzian age; and (3) a Murrumbidgee fauna, probably of early Couvinian age. The fauna of the Wellington Caves limestone has no species clearly diagnostic of any of these, but is possibly Lower Devonian. Five new species are described, and one species is re-described.

Most of the material studied consists of thin sections cut at the University of Sydney by Mr. H. G. Gooch from specimens collected by Misses E. Basnett, M.Sc., and J. Colditz, B.Sc., while the remainder consists of specimens and thin sections in the Australian Museum and the University of Queensland.

The lists of Rugose corals obtained from the various localities are as follows. Those marked * have been determined from externals only, and unless otherwise indicated, the remainder have been determined from thin sections.

A. Por. 10, Par. Nanima. *Tryplasma lonsdalei* Eth., *T. lonsdalei* var. *scalariforme* Eth. (both records from Etheridge, 1907), *Spongophyllum ? shearsbii* (Chapman; Hill, 1940*b*, p. 408), *Halysites* sp. (oral communication from Misses Basnett and Colditz). This locality has been referred to as 5 (or 5¼) miles from Wellington on the Gulgong (or Mudgee) road.

B. Por. 23, Par. Calwadgere. *Halysites* sp.

C. Por. 241, Par. Mickety mulga. *Propora* sp.

D. Por. 30, Par. Gundy. (7 miles from Wellington on the Arthurville road). **Rhizophyllum enorme* Etheridge (Hill and Jones, 1940, p. 182), "*Cystiphyllum*" sp. (Hill and Jones, 1940, p. 183) (Plate IV, fig. 2), "*Cystiphyllum*" *conjunctum* sp. nov. (Plate IV, fig. 3), *Disphyllum mesa* sp. nov., **Pseudamplexus princeps* (Etheridge; Hill and Jones, 1940, p. 185), *Tryplasma ? lonsdalei* Etheridge (Hill, 1940*b*, p. 406) (Plate IV, figs. 9*a*, *b*).

E. Fingerpost, Junction of Parkes and Arthurville Roads, Pors. 172, 166, Par. Curra. "*Cystiphyllum*" sp., *Disphyllum mesa*, **Tryplasma ? wellingtonense*, *Pseudamplexus princeps*.

F. Por. 42, Par. Wooroobooomi. *Radiophyllum* aff. *arborescens* (Hill and Jones; Hill, 1942*b*, p. 17) (Plate IV, fig. 8).

G. Por. 87, Par. Ponto. *Tryplasma* or *Pycnostylus* sp.

H. Limestone at turn-off of Caves Road from Wellington-Molong road. *Acanthophyllum* cf. *mansfieldense* (Dun; Hill, 1939*b*, p. 223) (Plate IV, fig. 1), *Tryplasma columnare* Etheridge (Hill and Jones, 1940, p. 187).

I. "WELLINGTON" (i.e., probably Wellington Caves). *Acanthophyllum* cf. *mansfieldense*, *Tryplasma wellingtonense* Etheridge.

J. WELLINGTON CAVES RESERVE, POR. 172, PAR. WELLINGTON. "*Cystiphyllum*" sp., *Eridophyllum immersum* sp. nov., *Radiophyllum* aff. *arborescens* (Plate IV, fig. 7), *Tryplasma wellingtonense*, large solitary undetermined Rugosa, *Heliolites daintreei*, Wellington type.

K. POR. 105, PAR. NARRAGAL. *? Aulacophyllum* sp. (Plate IV, figs. 11*a*, *b*).

L. POR. 50, PAR. CURRA. *Eddastræa expansa* sp. nov., *Phillipsastræa aperta* Hill (1942, Tamworth paper), *Phillipsastræa* sp. with resemblances to *P. speciosa* Chapman and *P' linearis* Hill (1942, Tamworth paper), *Favosites bryani* Jones (Hill and Jones, 1940, p. 190), *F. allani* Jones (Hill and Jones, 1940, p. 189).

M. POR. 59 NEAR 39, PAR. GEURIE. **? Xystriphyllum ? dunstani*, **Pseudamplexus princeps*.

N. POR. 206, PAR. MICKETY MULGA. **Pseudamplexus princeps*, *Pleurodictyum* sp.

O. BETWEEN PORS. 206 AND 59, PAR. MICKETY MULGA. *Acanthophyllum* sp., **? Xystriphyllum ? dunstani* or *? mitchelli*.

P. POR. 82, PAR. MICKETY MULGA. *Pleurodictyum* sp.

Q. POR. 94, PAR. WELLINGTON. *Amphipora* sp.

R. WELLINGTON-DUBBO ROAD NEAR GEURIE, 12 MILES FROM WELLINGTON (Pors. 197 and 198, Par. Geurie). *Acanthophyllum æquiseptatum* Hill (1940*c*, p. 251) (Plate V, figs. 1*a*, *b*), the specimen suggesting that this species is phaceloid, *Phillipsastræa speciosa* Chapman (Hill, 1939*b*, p. 237) (Plate V, figs. 8*a*, *b*).

S. POR. 62, PAR. MICKETY MULGA. *Acanthophyllum* cf. *æquiseptatum*.

T. "THE HOLMES" HOME PADDOCK, NEAR WELLINGTON. *Eridophyllum bartrumi* Allan (Hill, 1940*c*, p. 271).

U. POR. 247, PAR. MICKETY MULGA. *Xystriphyllum dunstani* (Etheridge, Hill, 1939*a*, p. 62) (Plate V, figs. 2*a*, *b*) (from Por. 13-247); *Disphyllum gemmiforme* (Etheridge; Hill, 1940*c*, p. 259) (Plate V, fig. 6), *Phillipsastræa oculoides* sp. nov., *Eridophyllum bartrumi* (Plate V, fig. 6), *? Grypophyllum ? aggregatum* Hill (1940*c*, p. 268) (Plate V, fig. 4).

V. POR. 247, PAR. MICKETY MULGA, NORTH OF ROAD. *Xystriphyllum magnum* Hill (1942, Tamworth paper) (Plate V, fig. 3).

A study of the lists shows that none of the localities is very rich in species; but a few have enough species already described for their ages to be deduced by comparison with other Australian faunas.

A. and B. are both said to contain *Halysites*, a genus which extends from the Upper Ordovician through the Silurian into the Gedinnian, so that a Gedinnian or pre-Devonian age is suggested for them; the appearance of *Spongophyllum ? shearsbii* and *Tryplasma lonsdalei* in A. suggests that this contains a representative of the Yass fauna, which is upper Wenlock or Ludlow. C. may be Silurian, for *Propora*, which it contains, is not known elsewhere above the Ludlovian.

The Garra fauna is recognised in localities D. and E. by the species *Rhizophyllum enorme*, "*Cystiphyllum*" sp., *Disphyllum mesa*, and *Pseudamplexus princeps*. Its age has been deduced to be Coblenzian (Hill, 1942*b*, p. 14) by comparison with the Mt. Etna fauna of Queensland. The limestone at F. has a specimen comparable with *R. arborescens* from the Garra and Mt. Etna faunas.

The Wellington Caves limestone (J.) contains one specimen comparable to this same Garra-Mt. Etna species, one species of a genus elsewhere Middle

Devonian (*Eridophyllum immersum*), and another of a genus elsewhere Silurian or Lower Devonian (*Tryplasma* sp.). Thus these suggest a Lower Devonian age. The limestone at H. is probably very close in age to the Caves limestone.

K. is either Silurian or Devonian, possibly Devonian, as *Aulacophyllum*, the genus to which one specimen is doubtfully referred, is known only in the Middle Devonian, although the family Pycnactidæ, to which it belongs, extends through Silurian and Devonian.

The fauna from L., Por. 50, Par. Curra, is comparable with that from the Loomberah limestone of the Tamworth district, which is possibly early Couvinian ; while the very few species from localities M. to Q. suggest that these are early Devonian in age, not younger than early Couvinian, and possibly Lower Devonian.

The Murrumbidgee fauna is represented in U., Por 247, Mickety mulga, by *Disphyllum gemmiforme* and *Eridophyllum bartrumi*, while the Sulcor fauna, which is not very dissimilar from the Murrumbidgee, is represented by the latter and *Xystriphyllum magnum*. The fauna of R. contains *A. æquiseptatum* of the Murrumbidgee and *P. speciosa* of the Loyola fauna. The age suggested by the group of localities R.-V. is thus early Couvinian.

Systematic Descriptions.

Only new species or those requiring revision are described. References to descriptions of other species have been given with the first entry of a specific name in the locality lists. The characters of most of the specimens from the Wellington district which belong to previously described species show very slight deviations from those of specimens from the type localities.

Family **Acanthophyllidæ** Hill, 1939*b*, p. 220 ; Tamworth paper, 1942.

Genus **Eddastræa** Hill, 1942, Tamworth paper.

Eddastræa expansa sp. nov. (Plate VI, figs. 5*a*, *b*.)

Holotype. 7290, Sydney University, Por. 50, Par. Curra, Wellington District, N.S.W. ? Early Couvinian.

Diagnosis. *Eddastræa* with few and very large corallites, with very wide dissepimentaria and dilated septa.

Description. The thamnastræoid corallum in the only two specimens known consists of two and three corallites, which are very large, about 40 mm. in diameter ; where they are in contact with one another, the corallites have no dividing epitheca ; the septa of neighbouring corallites are confluent, although in many cases they curve to meet at an angle. There are 36 major and 36 minor septa in a corallite 40 mm. in diameter ; the major septa are very long, and interdigitate in the tabularium, being turned aside in groups ; the minor septa are also very long, so that the tabularium is very narrow, only 6 mm. in diameter, and the dissepimentarium very wide, up to 17 mm. The septa are dilated, so that the interseptal loculi are but little wider than the septa ; irregular modification of the septa may occur at the periphery, some lateral dissepiments appearing, but usually there is a rough carination of the septal sides. The septa are carinate in the tabularium. The dissepiments are small and copiously developed, horizontally based at the periphery of the corallites and over their junctions, but very steeply inclined just near the tabularium. The tabular floors are concave with a median notch, and are formed of flat and close-lying tabellæ.

Remarks. The general morphology suggests that this species has arisen from a solitary *Acanthophyllum* of the *mansfieldense* type, which is characteristic of the Loyola limestone of ? Lower (possibly early Middle) Devonian age. No comparable compound species is known elsewhere.

Cystimorphs; Hill, 1939*b*, p. 248; 1942*a*, p. 241.

"**Cystiphyllum**" **conjunctum** sp. nov. (Plate V, figs. 3*a*, *b*.)

Holotype. 7291, Sydney University Collection, Por. 30, Par. Gundy, about 5 miles S.W. of Wellington. Coblenzian, Garra beds.

Diagnosis. Phaceloid "*Cystiphyllum*" with corallites up to 12 mm. in diameter, often connected by lateral outgrowths, with one or two series of large globose dissepiments, and without traces of septa.

Description. The corallum is phaceloid, the corallites being somewhat irregular in growth. They are up to 12 mm. in diameter, and may be connected laterally by broad outgrowths. The manner of increase has not been observed, nor the characters of the epitheca. Each corallite shows a very narrow peripheral stereozone, without trace of septa. There are one or two series of large, globose dissepiments, which give circular sections in transverse sections of the corallite; they show no septal bases. The tabular floors are flat or gently saucered, and are formed by complete tabulæ or by two or three rather globose tabellæ but little larger than the dissepiments.

Family **Disphyllidæ** Hill, 1939*b*, p. 224.

Genus **Disphyllum** de Fromentel; Hill, 1942*a*, p. 247.

Disphyllum mesa sp. nov. (Plate V, figs. 4, 5.)

Disphyllum præcox? Hill, 1940*b*, p. 399.

Holotype. 5276, Sydney University Collection, Por. 30, Par. Gundy, near Wellington. Coblenzian, Garra beds.

Diagnosis. *Disphyllum* with dilated septa, horse-shoe dissepiments, and mesa-shaped tabulæ.

Description. The corallum is phaceloid, and the corallites are slender, up to 6 mm. in diameter, though usually less, and rather distant, usually about 5 mm. apart; they may be in contact, and when close together they may be united by irregular lateral outgrowths. Typically the corallites are straight. Increase is peripheral and parricidal, but there is no common tissue developed in the axil between the new corallites. There are typically about 20 septa of each order; they are usually dilated in the dissepimentarium, and the dilatation may be so great that the interseptal loculi are closed; the major septa are long, reaching almost to the axis, but leaving a narrow axial space, into which only one extends. The minor septa extend about half-way to the axis. The dissepiments are very globose; they may consist of only one series of horse-shoe-like plates, the outer face inclining gradually to the epitheca and not turning back on itself like a true horse-shoe; or there may be an inner series of horse-shoe plates and an outer with the gradual inclination outwards; individual dissepiments are often difficult to distinguish when the septal dilatation is great. The tabular floors are in the shape of mesas, with a broad flat top and sloping sides; they may be formed by one complete tabula, or two or three elongate tabellæ; they are usually very close together.

Remarks. The species differs from *D. præcox* in the septal thickening and in the mesa-shaped tabulæ. It differs from *Thamnophyllum* by its possession of the mesa-shaped tabulæ, and by the absence of common dissepimental tissue in the axils of the branches. In its septal dilatation it resembles *Thamnophyllum* more than *Disphyllum*. The Upper Devonian European *D. minus* (Romer) is the only other species known to me with mesa-shaped tabulæ, and this has thinner septa than our form. In addition to the type locality, *D. mesa* occurs in the Garra beds of Curra Ck. crossing, Por. 172, Par. Curra, and on the road through Por. 166, Par. Curra.

Genus **Phillipsastræa** d'Orbigny ; Hill, 1939*b*, p. 236.

Phillipsastræa oculoides sp. nov. (Plate VI, fig. 9.)

Holotype. 5281, Sydney University Collection, Por. 247, Par. Mickety mulga, about 6 miles N.W. of Wellington. ? Early Couvinian.

Diagnosis. Partly aphroid *Phillipsastræa* with septa dilated at the inner parts of the dissepimentarium ; the inner row of dissepiments are horse-shoe-shaped but small.

Description. The corallum is massive, partly aphroid and partly astræoid. The tabularia are about 5 mm. in diameter and about 12 mm. apart from centre to centre. Each tabularium is surrounded by a fringe of dilated septal segments, the width of the fringe being about 3 mm. ; the septa do not often project into the tabularia, the major being but seldom longer than the minor ; there are about 16 septa of each order, equal in thickness ; outside the 3 mm. fringe the septa become discontinuous as a rule, only small thin discrete segments being left, but these may be traced outwards where they are seen to abut against those of a neighbouring corallite ; sometimes only dissepiments are to be found between the fringes of neighbouring corallites. Occasional discrete trabeculæ may be seen in the tabularia. The tabulæ are slightly concave or nearly horizontal, complete or incomplete. The innermost row of dissepiments is horse-shoe shaped, the remainder are inclined towards the neighbouring corallites ; they are larger in the outer series.

Remarks. In the aphroid corallum and the column of septal dilatation round the tabularium, this species resembles those formerly placed in the Upper Devonian *Pachyphyllum*, which, however, Lang and Smith regard as a homonym of *Phillipsastræa*. It is the only known Middle Devonian species with these characters.

Phillipsastræa sp.

S.U. 7276 from Por. 50, Par. Curra resembles *P. speciosa* Chapman (Hill, 1939*b*, p. 237) in the arrangement and size of the corallites, but there are only 10 septa of each order instead of the usual 13 or 14 of *P. speciosa*. In the number and somewhat also in the arrangement of the septa, the specimen is closer to *P. linearis* from the Sulcor limestone of the Tamworth district, but has thicker septa and the tabularia are very much closer together. More specimens are required for study from all these localities. The age indicated is Devonian, probably near the ? Lower (or Lower Middle) Devonian Loyola limestone.

Family **Entelophyllidæ** Hill, 1940*b*, p. 410 ; 1940*c*, p. 270.

Genus **Eridophyllum** Edwards and Haime ; Hill, 1940*c*, p. 270.

Eridophyllum immersum sp. nov. (Plate V, figs. 6*a*, *b*.)

Holotype. F.5612, now in the University of Queensland, to be transferred to the Australian Museum ; Wellington Caves limestone, Wellington Caves. ? Lower Devonian.

Diagnosis. Eridophyllum with dilated septa and with an occasional aulos, formed by the contact of the dilated axial ends of the septa.

Description. The corallum is apparently phaceloid, the corallites of the holotype, the only specimen known, being immersed in a stromatoporoid, and unequally spaced, from 0 to 9 mm. apart. They are from 2 to 10 mm. in diameter, with 20 septa of each order at a diameter of 7 mm. The septa are usually dilated so that the interseptal loculi are narrower than them ; their dilatation is greatest a little way in from the epitheca, then decreases gradually towards the axis ; where, in some corallites, the major septal ends may expand again

slightly, and contact one another to form a narrow vertical tube in the tabularium. Carination of the septa is rare and indistinct. The minor septa are a little over half as long as the major. The dissepiments form two groups; the outer, consisting of up to five series, is of very globose or even produced, horizontally based plates, larger than those of the inner group, which consists of up to seven series of very small, highly inclined plates. The tabular floors are domes with a deep axial insinking, and are formed of tabellæ arranged in three series; an outer series of plates sloping up from the dissepimentarium, an intermediate series of globose horizontally based plates, their inner slopes forming with the septal ends the narrow aulos, and an inner series of small, flat or slightly concave plates crossing the aulos.

Remarks. This species differs from others of the genus, which are Middle Devonian, in having dilated septa, with only rare or indistinct carination. The genus is known elsewhere in New Zealand, the U.S.A. and Canada.

Family **Pycnactidæ** Hill, 1940*b*, p. 401; 1942 Tamworth paper.

Genus **Aulacophyllum** Edwards and Haime; Hill, 1942, Tamworth paper.

? Aulacophyllum sp. (Plate V, figs. 11*a*, *b*.)

S.U. 7274 from Por. 105, Par. Narragal, has a tabularium 15 mm. wide in which septal dilatation is so great that the long major septa are almost in contact laterally, and a dissepimentarium up to 7 mm. wide in which the 40 major and 40 minor septa are thin. The tabular floors are flattened domes, formed of rather large globose tabellæ, and the dissepiments are small, numerous and steeply inclined. These characters are those of the Pycnactidæ, and in particular of *Aulacophyllum*, but the specimen lacks the axial space characteristic of *A. trizonatum*, the only species described as yet from Australia. The major septa reach the axis, and also are somewhat rotated in three of the quadrants. If the genus is correct, the age suggested is Devonian, but there is insufficient material for a complete understanding. The family is Silurian and Devonian.

Family **Rhabdocyclidæ** Hill, 1940*b*, p. 404.

Genus **Tryplasma** Lonsdale; Hill, 1940*b*, p. 405.

Tryplasma wellingtonense Etheridge. (Plate V, fig. 10.)

Etheridge, 1895, p. 160, pls. xxi, xxii, Wellington Caves; Etheridge, 1907, p. 89, pl. xvi, figs. 5-10; pl. xxi, figs. 11-12, pl. xxii, figs. 2-4. Possibly Lower Devonian.

Type Material. Not located; probably in Mining Museum, Sydney.

Diagnosis. Large solitary *Tryplasma* showing rejuvenescence and rootlets; and with long, thick rhabdacanthine septa, and irregular tabulæ.

Description. The corallum is solitary, large, trochoid, and curved, and may show changes in the direction of curvature. It may reach a diameter of 25 mm. in a height of 35 mm., when rejuvenescence may occur. Rejuvenescence may occur from an old calice, or may be of the type first entailing a decrease in diameter, as illustrated in Etheridge's figure, 1895, pl. xxi, fig. 1. The exterior of the specimens is beekitised, but traces of coarse longitudinal striation may occasionally be observed. There are about 30 septa of each order, each consisting of a series of very large and thick rhabdacanths directed upwards and inwards from the epitheca; the major septa reach nearly half-way to the axis, and the minor septa are a little shorter and thinner. The tabulæ are rather irregular; they may be complete, when they are nearly horizontal, or they may be incomplete, when the outer tabellæ slope down from the epitheca to meet an older inner tabula or tabella.

Acknowledgments.

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References.

Etheridge, R., Jr., 1895. An Undescribed Coral from the Wellington Limestone, N. S. Wales. *Rec. geol. Surv. N.S.W.*, **4**, pp. 160–162, pls. XXI–XXII.

———————— 1907. A Monograph of the Silurian and Devonian Corals of New South Wales. Part II. The Genus *Tryplasma*. *Mem. geol. Surv. N.S.W. Palaeont.*, No. 13, pp. 41–102, pls. X-XXVIII.

Hill, D., 1939*a*. The Middle Devonian Rugose Corals of Queensland. I. Douglas Ck. and Drummond Ck., Clermont District. *Proc. roy. Soc. Queensl.*, **50**, pp. 55–65, pls. IV, V.

———— 1939*b*. The Devonian Rugose Corals of Lilydale and Loyola, Victoria. *Proc. roy. Soc. Vict.*, (N.S.), **51**, pp. 219–256, pls. XIII-XVI.

———— 1940*b*. The Silurian Rugosa of the Yass-Bowning District, N.S.W. *Proc. Linn. Soc. N.S.W.*, **65**, pp. 388–420, pls. XI-XIII.

———— 1940*c*. The Lower Middle Devonian Rugose Corals of the Murrumbidgee and Goodradigbee Rivers, N.S.W. *J. Proc. roy. Soc. N.S.W.*, **74**, pp. 247–276, pls. IX-XI.

———— 1942*a*. The Middle Devonian Rugose Corals of Queensland. III. Burdekin Downs, Fanning R., and Reid Gap, North Queensland. *Proc. roy. Soc. Queensl.*, **53**, pp. 229–268, pls. V-XI.

———— 1942*b*. The Lower Devonian Rugose Corals from the Mt. Etna Limestone, Qld. *Proc. roy. Soc. Queensl.*, **54**, pp. 13–22, pl. I.

———— 1942*c*. The Devonian Rugose Corals of the Tamworth District, N.S.W. *J. Proc. roy. Soc. N.S.W.*, **76**, pp. 142–164, pls. II-IV.

Hill, D., and Jones, O. A., 1940. The Corals of the Garra Beds, Molong District, New South Wales. *J. Proc. roy. Soc. N.S.W.*, **74**, pp. 175–208, pls. II-VIII.

Explanation of Plates.

Plate V. Early Devonian Rugosa from the Wellington District.

All figures ×1·4 diameters approximately.

Fig. 1.—*Acanthophyllum* cf. *mansfieldense* (Dun.) U.Q. F.5611, limestone at turn-off of Caves road from Wellington-Molong road. Oblique section.

Fig. 2.—"*Cystiphyllum*" sp. S.U. 7294, Por. 30, Par. Gundy, Garra Beds. Coblenzian. Transverse section.

Fig. 3.—"*Cystiphyllum*" *conjunctum* sp. nov. Holotype. S.U. 7291. Por. 30, Par. Gundy, Garra Beds. Coblenzian. *a*, Transverse section, and *b*, vertical section.

Fig. 4.—*Disphyllum mesa* sp. nov. Holotype. S.U. 5276 (*a*). Por. 30, Par. Gundy, Garra Beds. Coblenzian. Transverse section.

Fig. 5.—*Disphyllum mesa* sp. nov. U.Q. F.6210. Wellington District. Coblenzian. Vertical section.

Fig. 6.—*Eridophyllum immersum* sp. nov. U.Q. F.5612. Wellington Caves limestone, Wellington Caves. *a*, Transverse, and *b*, vertical section.

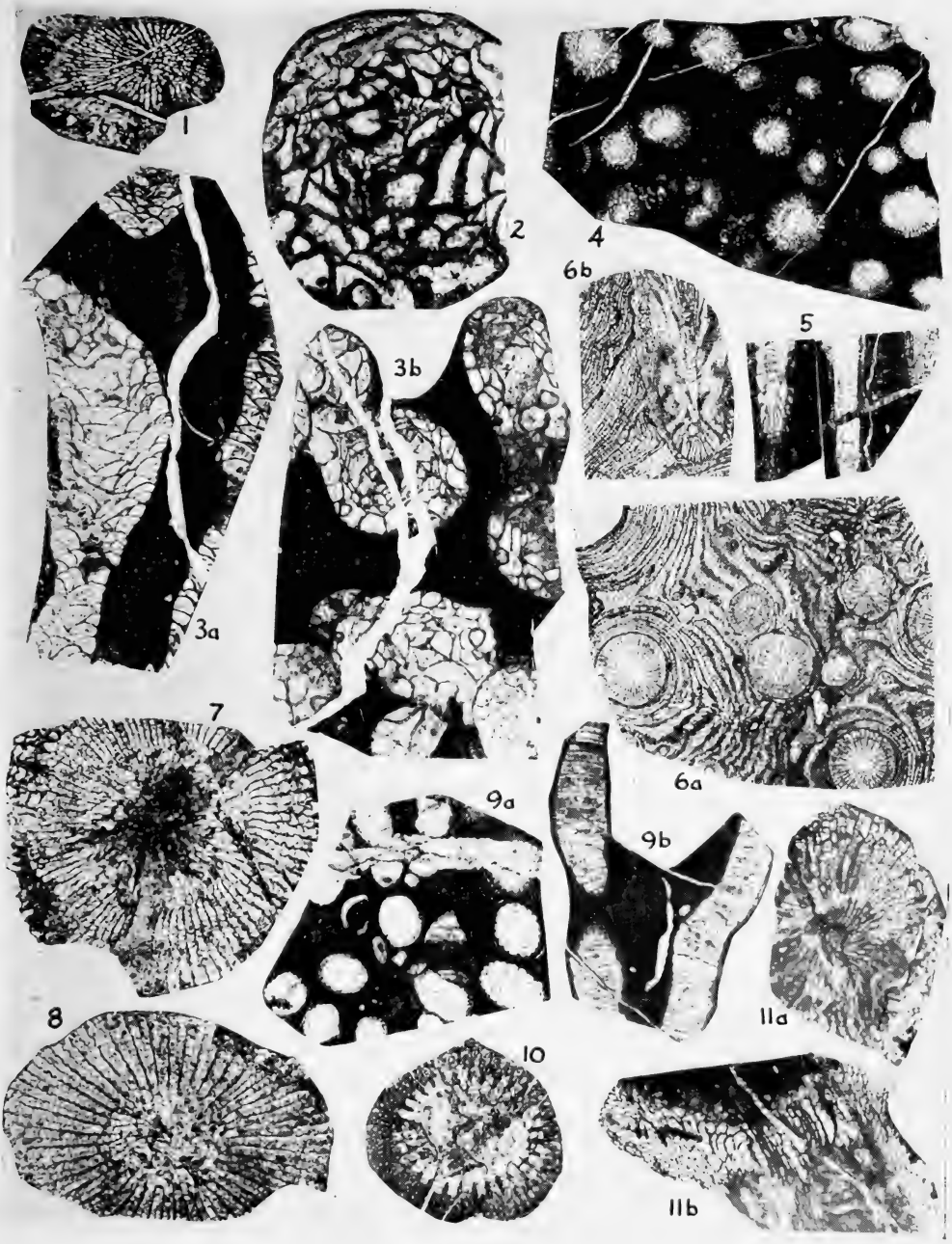
Fig. 7.—*Radiophyllum* aff. *arborescens* (Hill and Jones). S.U. 7295, Wellington Caves limestone, Wellington Caves. Transverse section.

Fig. 8.—*Radiophyllum* aff. *arborescens* (Hill and Jones). S.U. 5291, Por. 42, Par. Wooroboomi. Transverse section.

Fig. 9.—*Tryplasma ? lonsdalei* Etheridge. S.U. 7296, Por. 30, Par. Gundy, Garra Beds. Coblenzian. *a*, Transverse, and *b*, vertical section.

Fig. 10.—*Tryplasma wellingtonense* Etheridge. A.M. F.5687. Wellington. Transverse section.

Fig. 11.—*? Aulacophyllum* sp. S.U. 7274, Por. 105, Par. Narragal. *a*, Transverse, and *b*, vertical section.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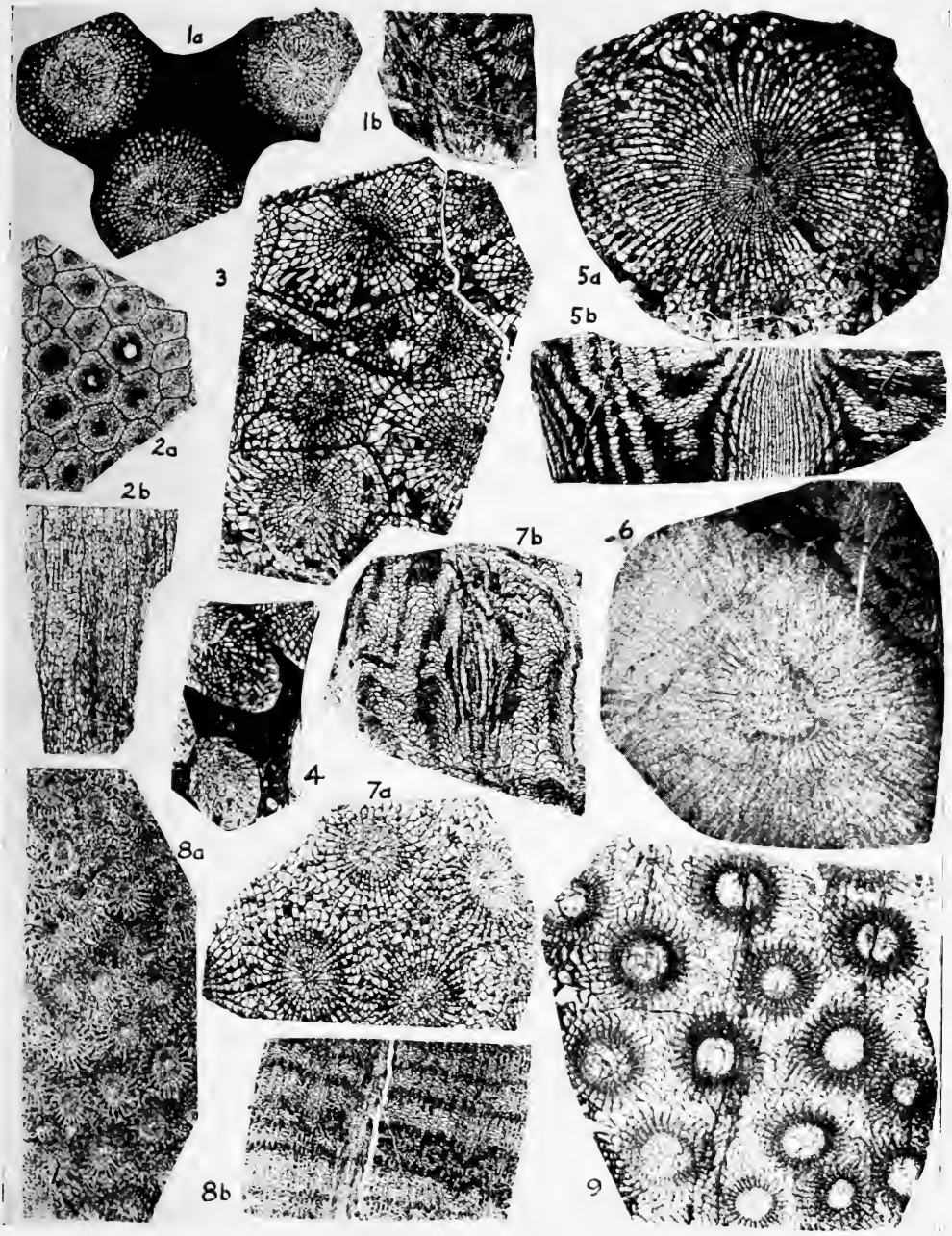
1a
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2b
7b
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7a
8a
8b
9

PLATE VI. MURRUMBIDGEE (COUVINIAN) RUGOSA FROM THE WELLINGTON DISTRICT.

All figures ×1·4 diameters approximately.

Fig. 1.—*Acanthophyllum æquiseptatum* Hill. S.U. 7297, near Geurie, 12-mile post from Wellington towards Dubbo. *a*, Transverse, and *b*, vertical sections.

Fig. 2.—*Xystriphyllum dunstani* (Etheridge). S.U. 5282 (*a*), Por. 39–247, Par. Mickety mulga. *a*, Transverse, and *b*, vertical section.

Fig. 3.—*Xystriphyllum magnum* Hill. S.U. 5292, north of road, Por. 247, Par. Mickety mulga. Transverse section.

Fig. 4.—*? Grypophyllum ? aggregatum* Hill. S.U. 5293 (*b*), north of road, Por. 247, Par. Mickety mulga. Transverse section.

Fig. 5.—*Eddastræa expansa* sp. nov. Holotype, S.U. 7290, Por. 50, Par. Curra. *a*, Transverse, and *b*, vertical section.

Fig. 6.—*Eridophyllum bartrumi* Allan and *Disphyllum gemmiforme* (Etheridge). S.U. 5278, north of road, Por. 247, Par. Mickety mulga. Transverse section.

Fig. 7.—*Phillipsastræa aperta* Hill. Holotype, S.U. 7289, Por. 50, Par. Curra. *a*, Transverse, and *b*, vertical sections.

Fig. 8.—*Phillipsastræa speciosa* Chapman. S.U. 7298, Wellington-Dubbo road, near Geurie, 12 miles from Wellington. *a*, Transverse, and *b*, vertical section.

Fig. 9.—*Phillipsastræa oculoides* sp. nov. Holotype, S.U. 5281 (*b*), Por. 247, Par. Mickety mulga. Transverse section.

SOME THERMOCHEMICAL PROPERTIES OF THE TORBANITE OF THE GLEN DAVIS DEPOSIT.

By R. F. Cane, M.Sc., A.A.C.I.

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Introduction.

The property of oil shale which renders it a valuable and interesting material both to the scientist and to the industrialist is that, on the application of heat, the organic matter decomposes into substances of lower molecular weight; these include all phases, liquids, solids and gases. In order to achieve an effective retorting of the shale it is necessary, in the first place, to have a clear understanding of the reactions which occur during the retorting process, and of the physical and thermochemistry of the shale pyrolysis. Very little is known of the mechanism of the reactions occurring here, chiefly because of the fact that the structural chemistry of the kerogen molecule is practically unknown. The conditions existing during the relatively small temperature interval in which the kerogen molecule decomposes render it absolutely essential to have exact information on the magnitude of the quantities involved during this transformation.

The torbanites occurring in the Upper Coal Measures of Permian age vary in colour from black with a satin-like lustre, in the case of a rich shale, to greyish rock in the inferior quality seams. These two extremes vary in oil yield from 210 gallons per ton (specific gravity 1·04) to 30 gallons per ton (specific gravity 2·31). It is unnecessary to give here a lengthy description of the physical and microscopic structure of the torbanite in this region, as this has already been given excellent treatment by Dulhunty (1941).

The principal changes in the microstructure of these torbanites can be summarised briefly as follows: up to 350° C., no apparent changes are produced in their chemical structure, but the mechanical properties alter to a slight extent, for instance their bending moment decreases, and speaking generally they become "weaker" in strength. As the temperature approaches 400° C., the organic cell structure of the shale begins to disintegrate. This increases with temperature until 450° C. is reached, when the cell structure has completely disappeared.

The Nature of the Thermal Decomposition.

In order to investigate the mechanism of the reactions occurring during the decomposition of oil shale, a small reaction vessel was built, consisting of 1 in. seamless pipe with flanged ends. One end was fitted with a thermocouple well and the other end to a pressure gauge system. The first stage in this phase of the investigation was to find the amount of pressure generated by the shale during the different stages of decomposition and, from the application of the gas laws, to determine whether any appreciable amount of gas was evolved before the true pyrolysis, and so ascertain whether the incipient formation of the precursor to decomposition was purely a molecular rearrangement or the first stage in the breakdown. The vessel was charged with granulated shale and the temperature gradually increased until the pressure reached about 20 lb. per sq. in., whereupon the vessel was cooled, the flanges opened and the

nature of the product investigated. This was a most interesting phase of the work, as whilst still hot, the shale, after having undergone the above treatment, was practically in the liquid phase, resembling a mixture of liquid bitumen and molten rubber.

Following the removal of water vapour and occluded gases, the first stage of the decomposition is marked by the evolution of carbon dioxide and hydrogen sulphide. This occurs at comparatively low temperatures, and denotes the initial steps of the transformation into the intermediate bitumen. It is impossible to state the lowest temperature at which this " depolymerisation " will occur, as results showed at least minute traces at temperatures approaching 300° C. and even oil formation at 360° C., after about three hours' heating. However, at 360° C. it was shown that relatively little gas is generated during the first stages of decomposition and that the large volumes of gas met with during the retorting of shale arise, not from the decomposition of the kerogen, but from the subsequent cracking of the pyrobitumen to oil. This pyrobitumen appears to be the real origin of the crude oil. The physical properties of this substance are entirely in contrast to those of the original oil shale ; for example, the shale is tough, rigid and insoluble in most organic solvents, whereas the resulting bitumen was of a rubber-like texture and practically entirely soluble in solvents such as benzene.

It appears that the original organic matter of the shale is not the true oil producing body, but this organic matter changes, at a temperature lower than that necessary to produce oil, into the abovementioned bitumen. Normal shale which has not been treated by heat in any way is solid, hard to fracture, and practically insoluble in the normal organic solvents (some cyclic ketones, such as cyclo-hexanone, appear to be the best solvents), but after it has been heated in the region of 380° C. a remarkable structural change occurs, whereupon the shale changes into a gummy semi-liquid mass.

The decomposition of the kerogen in oil shale is regarded by many as occurring in steps, as in the distillation of crude oil, so that, during pyrolysis, the first oil produced must necessarily be of lower specific gravity than the later fractions. However, results showed that after its formation the bitumen decomposes and yields, simultaneously, the whole series of products varying from the lightest to the heaviest. It has been shown that the crude oil does not vary appreciably in gravity as the retorting process goes on to completion, and it may be assumed that each kerogen molecule acts independently as a potential producer of oil, gas and coke.

A sample of shale was slowly retorted, and samples of the liquid products of decomposition collected over equal intervals of temperature, as measured in the shale mass. A determination of specific gravity was carried out on each sample. A microdistillation showed that all fractions contained " light ends ". These results are illustrated in Table I.

TABLE 1.

Temperature Range of Retorting ° C.	Specific Gravity of Oil at 20° C.
–450	0·88
450–470	0·89
470–480	0·89
480–490	0·90
490–500	0·90
500–510	0·90
510–520	0·90
520–530	0·90
530–540	0·91
540–550	0·92
550–	

Thus it can be seen that the retorting of shale resolves itself into the conversion of the organic matter into the bitumen, and the subsequent cracking (at atmospheric or slightly subatmospheric pressure) of this bitumen into crude oil, naphtha, gas, etc. Taking this point of view, the lighter fractions may then be regarded as having no origin in the shale at all, but are produced by the cracking of the " nascent " crude oil under the conditions existing in the retort at the time of their formation. This does in some way explain the great variability in the properties of the crude oil produced from the same shale under various retorting conditions. Hence, the retort must be regarded, not as an oil-producer, but as a bitumen former (i.e., the transformation of the organic matter in the shale into the heavy bitumen-like product mentioned above). This having taken place, the retort from then onwards is simply acting as a cracking still. This is emphasised by the fact that shale oils are highly unsaturated, and in this way resemble cracked pressure distillates from flow oils.

The Rate of Pyrolysis.

Rate of pyrolysis of shale is an important factor in determining the kinetics of the removal of gases and vapours from the shale. The rate of pyrolysis was determined experimentally in the apparatus outlined below.

A piece of channel iron 18 by 7 by 3 inches, upon which was welded a bar of iron approximately 15 by $\frac{3}{4}$ inches, served as the base of the apparatus. Between the end lugs was strung a length of piano wire, in which tension was maintained by two end screws. At the mid-point of this wire, and at right angles to each other and to the wire, two cross members were brazed, the horizontal member of which was 8 inches long and served to carry the shale sample. The upright member was 2 inches long and carried a small mirror. From the end of the horizontal member a small balance pan was hung by means of a thin steel wire. The whole set-up resembled a torsion balance. The procedure was as follows.

A tubular furnace, closed at both ends except for a small hole for the suspension wire, was set in an upright position, and into it the shale sample contained on the balance pan was hung, and the maximum torsion produced in the piano wire was determined by measurement of the deflection of an optical beam, reflected from the small mirror attached to the upright. The furnace was preheated to the required temperature and the interior filled with an inert gas, and the rate of decrease of mass of the shale was measured by the decreasing deflection of the optical beam as measured on a scale. The experiment was discontinued when constant deflection denoting complete carbonisation was obtained. The set-up was then calibrated by putting known masses on the pan and calibrating the scale reading. A series of experiments was carried out with the apparatus above described, the results obtained being interpreted by means of graph (see Figs. 1 and 2).

These results showed clearly that the rate of pyrolysis was a function of the particle size.

Two series of determinations were carried out, at 400° C. and 450° C. A series of test blocks were cut from " first quality " shale by means of a rotating aluminium disc fed with carborundum powder ; these were, as far as could be maintained, in arithmetical progression as regards linear dimensions, the smallest one being approximately one centimetre cube (see curves 1, 2, 3 and 4 in Figs. 1 and 2).

Qualitative Examination of the Shale Pyrolysis.

In order to determine experimentally whether the shale pyrolysis was an endothermic reaction, as might at first be imagined, several experiments were carried out with this aim in view. Following the work of Hollings and Cobb

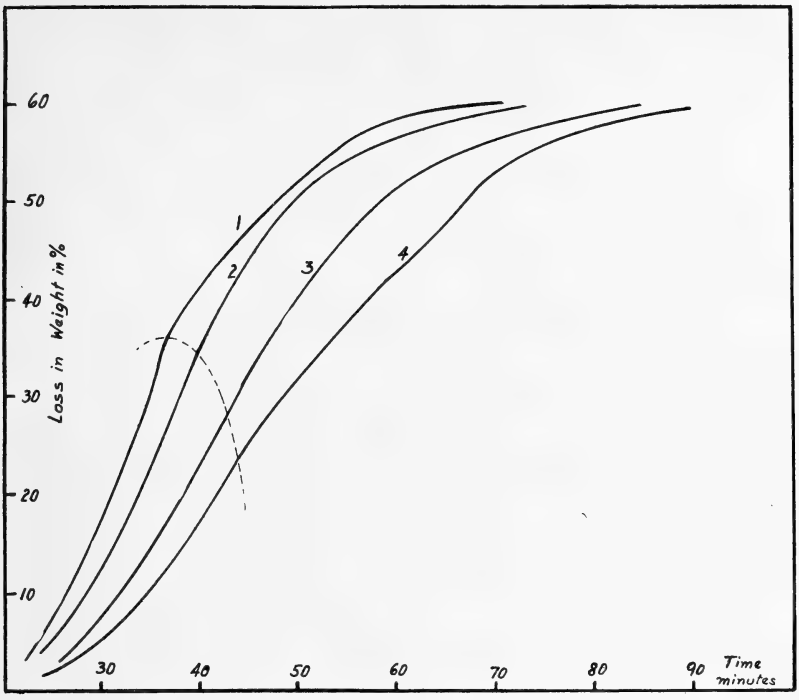

Fig. 1.—Rate of Pyrolysis. Temperature 400° C.

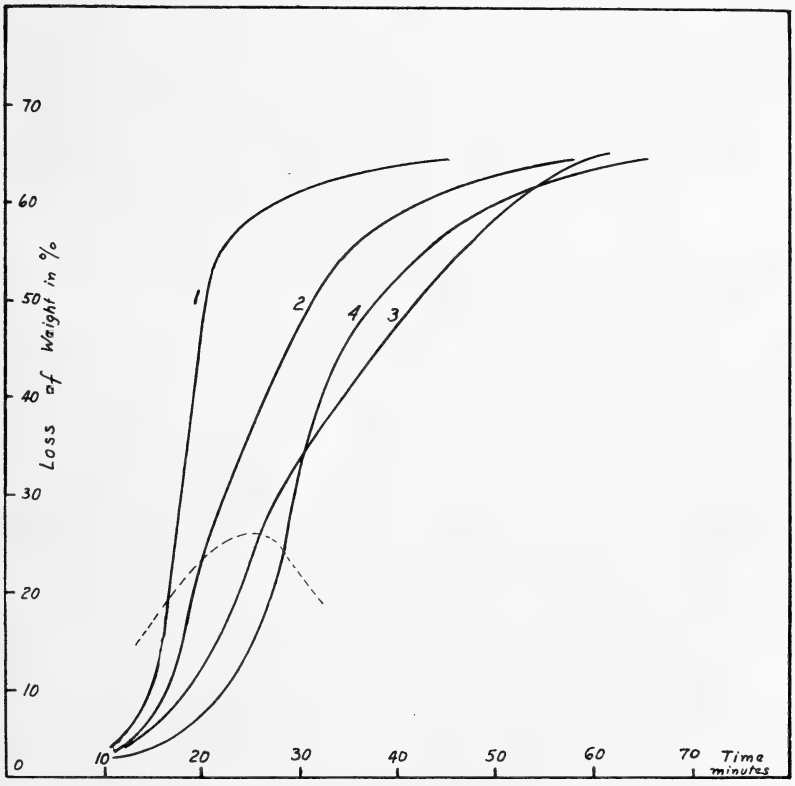

Fig. 2.—Rate of Pyrolysis. Temperature 450° C.

(1915), the following set-up was arranged : An iron tube 1 inch in diameter was clamped concentric to the wall of a furnace and in it two silica tubes were clamped running parallel to one another, resting inside the iron tube. Two thermocouples were placed in the silica tubes, so as to constitute a differential thermocouple. The silica tubes were lightly packed with dehydrated Fuller's earth, the temperature of the furnace gradually raised, and any deflection of the galvanometer connected to the differential thermocouple noted. Two parallel experiments were carried out, in which one of the silica tubes was packed with dry powdered shale. Should the reaction occurring during the pyrolysis of the shale mass be definitely exo- or endo-thermic, such direction of reaction would show up in the galvanometer deflection. Results of this phase of the work are shown in Fig. 3.

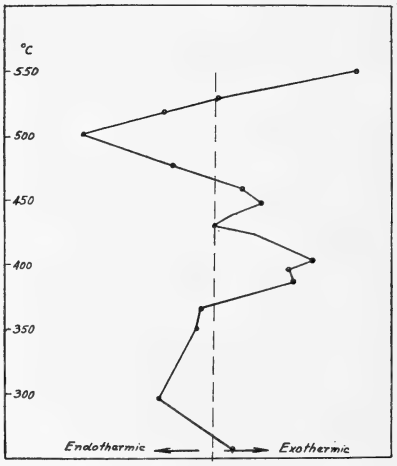

Fig. 3.—Thermal Reactivity of Shale.

It can be seen that the direction of the reaction is by no means regular, and in this respect is similar to other shales, and to coal. [See McKee (1925) and Luts (1935).]

In relation to Fig. 3, the following remarks should be made. The sulphur and oxygen containing compounds are the first to decompose with exothermic reaction, producing carbon dioxide, hydrogen sulphide and water vapour. Apparently the hydrocarbons at once commence to crack with an endothermic reaction. Owing to the low thermal conductivity and high end temperature necessary for the complete decomposition of the contained organic matter, some cracking of the oil vapours to fixed gases will occur, and a certain amount of fixed carbon is to be expected at the end of the pyrolysis. Furthermore, in commercial practice, as it is necessary to raise the temperature of the shale well above this temperature (380° C.), we can expect a greatly accelerated rate of cracking even in the most gentle of retorting operations. The relation given by von Strache (1922) between the amount of contained oxygen and the heat of low temperature carbonisation is that heat of reaction increases with the increase of oxygen ; but with a very small oxygen content the heat of reaction is negative. The overall direction of the reaction may be found from the difference in heat values of the gas, oil and coke, and the heat of combustion of the shale. From this consideration Constan and Kolbe (1908) have found that the reaction is 7·2% exothermic for ichthyol shales.

Thermal Expansion of Shale Oil.

The coefficient of thermal expansion was determined by measuring the expansion of a known volume of the liquid when raised from one temperature to another under closely controlled conditions. It has been shown that the coefficient of thermal expansion varies inversely as the specific gravity between approximately 0·001 for naphtha and 0·0008 for crude oil. The results obtained gave close agreement with those of the A.S.T.M. specifications for flow oil, and showed that these tables may be used for gravity corrections for shale oil. Table 2 shows the mean coefficient of thermal expansion between 20° C. and 60° C. for oils of different specific gravity.

Table 2.

Specific Gravity.	Coefficient of Expansion.
0·781	$10{\cdot}66 \times 10^{-4}$
0·794	10·41
0·804	10·07
0·825	9·66
0·843	9·13
0·868	8·60
0·883	8·26
0·895	7·94

From this table a chart may be constructed from which a system of specific gravity correction factors may be obtained.

Viscosity of Shale Oil.

The effect of constitution on viscosity is too complex a subject to be treated here, and no formulæ have been found to be entirely satisfactory in this application. However, broadly speaking it is found that, in the case of complex hydrocarbon mixtures, the viscosity varies with the specific gravity, together with another factor, and several relationships have been put forward connecting viscosity with specific gravity and/or other constitutional properties.

In the case of crude shale oil, it is found that a rough linear relationship exists between viscosity and specific gravity as indicated in Table 3. The results were determined with an Ostwald pipette viscometer under isothermal conditions at 100° F. The individual figures were interpolated from a graph resulting from many determinations over a long period of time. This table also shows the variation in viscosity with change of temperature of a typical crude oil, giving a viscosity index of approximately 150.

Table 3.

Specific Gravity at 20° C.	Viscosity. Centistokes at 100° F.	Viscosity Centistokes at t° C.	Temperature t° C.
0·87	5·7	16·0	30
0·88	8·4	10·8	40
0·89	11·1	7·5	50
0·90	13·9	5·5	60
0·91	16·6	4·2	70
0·92	19·3	3·3	80

The Specific Heat of Oil Shale.

The specific heat of oil shale can be determined experimentally by the normal method of mixtures. However, owing to the varying composition of the shale and the varying amount of inorganic matter contained therein, one value will not suffice to cover all samples of shale. Employing the results of Dulong and von Kopp on the additive character of the specific heats, a theoretical approach

may be made and the specific heat of the pure organic and inorganic matter in shale may be determined. The composition of a representative sample of the ash from the Glen Davis deposits is shown in Table 4.

Table 4.

Chemical Composition.	Percentage.	Specific Heat.	Product.
SiO_2	67·3	0·191	12·85
Fe_2O_3	3·9	0·155	0·60
Al_2O_3	22·0	0·184	4·05
CaO	0·9	0·181	0·16
MgO	0·5	0·220	0·11
SO_3	2·6	0·18	0·47
Alkaline oxides ..	2·8	0·2	0·56
			18·80

Specific heat of the shale ash : 0·19 cal./grm./° C.

The specific heat of the organic matter in oil shale may be approximated in the same manner from the percentage composition of the kerogen and the atomic heats of the constituent atoms (see Table 5).

Percentage Composition :

Table 5.

C = 85·1%. H = 10·6%. S = 0·5%. N = 1·3%. O = 2·3%.

Analysis Percentage.	Atomic Heat.	Atomic Weight.	Percentage × Atomic Heat / Atomic Weight.
C : 85·1	1·76	12	12·5
H : 10·6	2·3	1	24·38
S : 0·5	5·54	32	0·09
N : 1·3	3·42	14	0·32
O : 2·5	3·48	16	0·54
			37·8

Specific heat : 0·38 cals./grm.

Thus for dry shale with 50% mineral matter the theoretical specific heat of the sample would be $\frac{0·38 + 0·19}{2} = 0·28$ cals./grm. For American shales, values shown in Table 6 have been found.

Table 6.

Shale from De Beque..	0·265	McKee and Lyder (1922).
Shale from Parachute	0·242	U.S. Bureau of Mines (Gavin and Sharp, 1920).
De Beque	0·273	,, ,, ,, ,,
Shale residue	0·223	,, ,, ,, ,,
De Beque	0·280	McKee and Lyder (1922).

Thus it can be seen that the specific heat increases with increasing " richness " of the shale and varies between the theoretical limits found above.

The specific heat of the moisture-free shale was found experimentally by the usual method of mixtures, using an adiabatic calorimeter. It was found that water was not a good cooling medium because of the fact that there was no effective " wetting " of the surface of the shale. Some organic liquids were found to be more effective in this direction, carbon tetrachloride and nitrobenzene being used. The results obtained are given in Table 7.

Table 7.

Sample Number.	Ash Percentage.	Specific Heat. (Observed.)	Specific Heat. (Calculated.)	Temperature Range. ° C.
14	22·2	0·318	0·336	20–50
7	32·3	0·301	0·316	30–80
23	56·4	0·278	0·271	20–50
42	86·2	0·242	0·214	20–50

By interpolation of these results the specific heat of a shale with a known ash content may be found.

The Specific Heat of Shale Oil.

The functional relationship between specific heat and specific gravity has not been satisfactorily determined in the case of complex hydrocarbon mixtures. The specific heat of most crude oils is approximately 0·5 grm. cals./grm./°C. and agree with the general equation

$$Cp = a + bt + ct^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where $a = 0{\cdot}5$ and $b = 0{\cdot}001$.

t = temperature in °C.

The specific heat of petroleum oil has been determined by Kraussold (1932), who suggested the equation $Cp = 0{\cdot}5 + 0{\cdot}0011\ (t\text{–}20)$. From experimental work on crude shale oil from the Glen Davis torbanites it has been shown that Kraussold's formula is only approximate, and a better relationship is

$$Cp = 0{\cdot}503 + 0{\cdot}00118\ (t\text{–}20) \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Assuming that the variation is linear over a limited temperature range, we may substitute "a" in formula (1) by a function of the specific gravity of the form $\frac{K}{(\text{Sp. gr.})^n}$, where K is a constant and n is a number less than 1.

A suggested equation is:

$$Cp = \frac{0{\cdot}4915}{(\text{Sp. gr.}_{20})^{0{\cdot}1}} + 0{\cdot}00118\ (t\text{–}20)$$

It is interesting to compare this equation with that suggested by Kraussold for flow oil,

$$Cp = \frac{0{\cdot}425}{(\text{Sp. gr.}_{15})^{\frac{1}{2}}} + 0{\cdot}0011\ (t\text{–}20)$$

Heat of Combustion of Oil Shale.

Heat of combustion was determined by igniting a known mass of the shale in a Parr oxygen calorimeter, in which the sample is burnt in an atmosphere of oxygen under 20 atm. pressure. The charge is ignited by means of a small fuse wire and the heat generated is absorbed in water in the usual manner. If samples showed traces of free carbon after ignition, the results were discarded. The results obtained are given in Table 8.

Table 8.

Sample No.	16A	14	18A	23	20A	51
Heat of combustion (cals./grm.) (corrected)	7,804	7,651	5,739	3,818	3,150	2,317
Ash (per cent.)	21·1	22·2	24·03	59·09	61·52	76·2

This, by extrapolation, gives a value of 10,680 grms./cals. for the calorific value of pure kerogen.

Corrections for Fuse Wire.

The sample in the bomb is ignited by a fuse wire which is partially consumed during the combustion. The amount of wire taking place in the combustion is determined and a correction of approximately 2·8 calories per centimetre of burned wire is then applied.

Correction for Acid.

Since the combustion in the bomb takes place in an atmosphere of pure oxygen, there is a better chance of complete oxidation than under normal conditions. For example, in the normal oxidation of sulphur compounds sulphur dioxide is produced. However, under the conditions existing in the bomb at the time of the explosion there are appreciable amounts of sulphur trioxide produced which, in the presence of water vapour, form sulphuric acid. As this is an exothermic reaction, some correction must be applied to compensate for it. The calculations are based on the assumption that all the acid is in the form of nitric acid, rather than to attempt to separate the two acids. However, the heat liberated by the formation of sulphuric acid is greater than that liberated by the formation of a corresponding amount of nitric acid, and it becomes necessary to apply another correction for the heat generated above that accounted for in the acid correction. This is the Sulphur Correction. Approaching this, as previously, from the theoretical angle, we may arrive at the following calculation :

Assuming $C + O_2 \rightarrow CO_2 + 94{,}380$ grm. cals. per 12 grams C
$H + \frac{1}{2}O \rightarrow \frac{1}{2}H_2O + 34{,}190$ grm. cals. per 1 gram H
$N + O_2 \rightarrow NO_2 - 7{,}400$ grm. cals. per 14 grams N
$S + O_2 \rightarrow SO_2 + 69{,}300$ grm. cals. per 32 grams S

and taking the empirical composition of typical torbanite of this deposit as :

C = 85·1%.
S = 0·5%.
N = 1·3%.
H = 10·6%.

gives a theoretical heat of combustion of 10,003 grm. cals. per grm. for pure kerogen.

Heat of Combustion of Shale Oil.

The heat of combustion of the liquid products of the pyrolysis were determined in a Parr oxygen bomb calorimeter using the same method as with the solid shale. Using different samples of oil, the following results were obtained :

Sample No.	8	17	21	14N	18N
Calorific value, gross (grams/cals.)	10,610	10,904	11,018	10,732	11,091

Mean value for liquid products of decomposition : 10,872 grm./cals.

This value may be checked approximately either by means of the characteristics of the oil in question or by means of the ultimate composition.

(i) From the characteristics of the oil.

Average values of the combustion characteristics of different oils have been tabulated, and representative values have been assigned to the heat of combustion when such data as gravity and distillation curve are known.

Assuming a specific gravity of 27° A.P.I. and " mean average boiling point " of 630° F., a calorific value of approximately 10,700 cals./grm. is given by tables published by Universal Oil Products Company of Chicago.

(ii) From ultimate composition.

Assuming an average analysis of the oil as

C = 86·3	S = 0·6
H = 11·3	O + N = 0·4

a theoretical value of 10,737 cals./grm. for the gross heat of combustion is obtained.

The Heat Necessary to Decompose a Known Mass of Shale.

The theoretical heat for the low temperature carbonisation of shale may be divided into the following sections :

1. The warming of the shale and contained moisture from room temperature to 100° C.
2. The heat of vapourisation of the water.
3. The heating of the shale from 100° C. to the point of decomposition.
4. The heat to decompose the shale.
5. The heat to volatilise the products of pyrolysis.

Various values have been found for these operations, varying from 190 cals./grm. for Estonian shales to 480 cals./grm. for American shales.

" Heat of Reaction " of the Shale.

By " heat of reaction " it must be understood that this term is not used in its common sense, but is meant to convey " the heat necessary to convert a given mass of shale into oil, gas and coke under standard conditions ".

The " heat of reaction " of the shale may be obtained by one of three methods :

1. Direct determination of the heat necessary for the pyrolysis, calculated from the application of the Stefan-Boltzmann Law, allowing for radiation and conduction and convection losses. However, owing to the great complexity of the equations involved, and the many assumptions that have to be made, this method of determining the heat necessary for the decomposition is not satisfactory in the present case.

2. By the use of Hess's Law it follows that, if we determine the heat for the complete oxidation of one gram of shale and subtract from that the heat evolved when the total products of pyrolysis are oxidised completely, the differences should be the amount of heat necessary to cause the above pyrolysis. It is realised that the heats involved on both sides of this equation are comparatively large and are quite large in relation to the difference between them (the quantity which we wish to determine), and consequently some errors may be introduced but this method, although approximate, gave the most reliable results.

3. Measurement of the heat necessary to cause shale pyrolysis by calorimetric methods. A quantity of heat slightly in excess of that needed for the pyrolysis is added to the shale under consideration, and that measured by suitable means.

Gray King Assay of the Shale to Determine the Heat Balance.

Two Gray King assays were carried out on a type sample of shale. The normal condensing system was replaced by a freezing mixture of solid CO_2, in which a U-tube was immersed. Every precaution was observed to see that the weight balance was as accurate as experimental details allowed. The Runs (5 and 6) were carried out under strictly controlled conditions, and the results are set out in Table 9.

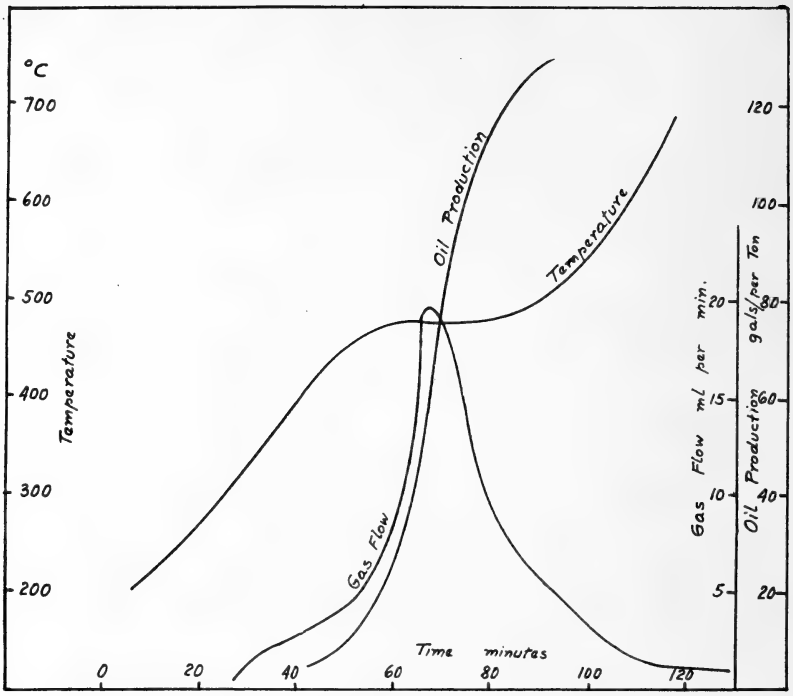

Fig. 4.—Gray King Assay of Shale.

TABLE 9.

Run No.	5	6
Weight of shale	10·314 grms.	11·131 grms.
Weight of coke	4·261 ,,	4·766 ,,
Weight of oil	5·510 ,,	5·595 ,,
Volume of gas—		
At 25° C. and 712 m.m.	557ml.	550 ml.
At S.T.P.	478 ,,	472 ,,
Weight of gas	0·547 grms.	0·552 grms.
Shale (per cent.)	100	100
Coke (per cent.)	41·31	42·82
Oil (per cent.)	53·42	52·26
Gas (per cent.)	5·30	4·96
	100·03	100·04

Analysis of the gas and coke produced during Run 6 showed the composition given in Table 10.

TABLE 10.

Composition of Gas.	%	Composition of Coke.	Run 5.	Run 6.
Acid gases	0·13	Volatile matter	8·14	10·58
Oxygen	0·17	Fixed carbon	29·95	27·12
Olefines	0·36	Ash	61·91	62·30
Ethylene	0·18			
Carbon monoxide	0·18			
Hydrogen	0·45			
Methane	1·70			
Ethane and higher paraffins ..	1·10			
Nitrogen	0·68			
	4·95		100·0	100·0

Heat Balance on Run 6.

Heat of Reactants:

Heat of combustion of the shale = 7211·8 cals./grm. (observed).

Heat of Products:

Coke—			
Volatile matter	10·58	4·53	406·6 cals.
Fixed carbon	27·12	11·61	1123·6 „
Ash	62·30	26·68	
	100·0	42·82	1530·2 cals.
Oil—			
Mean of three determinations		52·26%	5661 cals.
Gas—			
From gas analysis and calculation	472 ml.	4·95%	44·6 cals.

Heat Balance.

Shale .. .. Oil + Gas + Coke.
100 .. .. 52·26 + 4·96 + 42·82 (weight balance)
7212 .. .. 5682 + 45 + 1530 + R

R = 45 calories/grm. of shale.
= 86 cals./grm. of oil produced.

From the above results, which must be regarded as approximate only on account of the experimental errors involved, it may be seen that there is only a small quantity of heat transfer in the conversion of the shale into oil. The comparatively large amount of heat which is found to be necessary in the commercial retorting of shale is accounted for by heat losses and the low thermal conductivity of the shale.

The determination of thermal conductivity of shale is a matter of some difficulty in the present case as, owing to the low value of this characteristic, one face of the shale has to be maintained at a relatively high temperature, and this will always cause some decomposition. The thermal conductivity of American oil shale has been determined by McKee and Lyder (1922), for which they report a value of 0·00086 c.g.s. units. Winkler has recorded a result of 0·0005 as the thermal conductivity of Estonian oil shale, but he does not state whether it is air-dried or moisture free. As an interesting comparison, the following equations have been proposed by the International Conference in Pittsburgh in 1931 for the thermal conductivity of coals.

For a coking coal:

Thermal conductivity $= 0{\cdot}003 + 0{\cdot}0016 \times 10^{-3}t + 0{\cdot}0016 \times 6 \times 10^{-6}t^2$.

For a middle gravity coal:

Thermal conductivity $= 0{\cdot}003 + 0{\cdot}0013 \times 10^{-3}t + 0{\cdot}0015 \times 10^{-6}t^2$.

Cp. U.S. Bureau of Mines value = 0·0038 c.g.s. units [Gavin and Sharp (1920)].

Summary.

Several salient features of torbanite pyrolysis have been investigated, and it has been shown that the oil is produced by the decomposition of a semi-solid intermediate phase, and there is no direct conversion of the original organic matter into crude oil and gas. The nature of this reaction is by no means regular—the two controlling factors in the nature of the oil produced are time and temperature. Values have been found for the following properties of the crude oil obtained from Glen Davis torbanite, viz., thermal expansion, viscosity, specific heat and heat of combustion, and in most cases

values have been determined also for the torbanite or oil shale as it is generally known.

Acknowledgment.

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References.

Constan and Kolbe, 1908–1909. *Jour. fur. Gasbeleucht.*

Dulhunty, J. A., 1941. The Physical Effects of Heat on the Torbanites of New South Wales. *Proc. Linn. Soc.*, **66**, 335.

Gavin, M. J., and Sharp, L. H., 1920. Some Physical and Chemical Data on Oil Shales. *Oil and Gas Jour.*, **19**, 86.

Hollings and Cobb, 1915. *J. Chem. Soc.*, **107**, 1106.

Kraussold, H., 1932. The Specific Heat of Mineral Oil. Petroleum.

Luts, K., 1935. *Der Estlandische Brennschiefer.—Kukersite.* Tartu, **2**, 69.

McKee, R. M., 1925. Oil Shale. A.C.S. Monograph. New York, **4**, 78.

McKee, R. H., and Lyder, E. E., 1922. The Thermal Decomposition of Oil Shales. *Petroleum Times*, Nos. 160, 163, 164.

Methods of Analysis of Coal, 1927. *Dept. Sc. Ind. Res., Fuel Research Publication* 7.

von Strache, 1922. The Heat Necessary for the Dry Distillation of Shale. *Brennstoff Chemie*, **3**, 337.

MOVING SOURCES OF HEAT AND THE TEMPERATURE AT SLIDING CONTACTS.

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1. Introduction.

Problems involving moving sources of heat arise frequently in practice, notably in the calculation of temperatures at sliding or cutting contacts, but despite their importance they have not been studied systematically. One reason for this is the uncertainty of the nature of the contact, and another the very wide range possible in the numerical parameters; these facts practically limit mathematical discussion to numerical calculations for a particular model of a particular system, and make general discussion difficult. In this paper an attempt is made, in connection with the problem of plane sliding, to set out fully the assumptions made and the numerical consequences of the mathematical theory in a form in which it is hoped they can easily be used by experimenters to discuss particular models of sliding surfaces.

In §§2–9 the theory of uniform plane sources of heat of various shapes moving with constant velocity in the surface of a semi-infinite medium with no loss of heat from the surface is discussed. In §§4, 5 the temperatures attained in the plane of the source when the motion has gone on infinitely long are given, and in §6 the way in which these temperatures build up is considered. The temperatures within the medium are calculated in §7. The maximum and average steady temperatures over the area of the source are collected in §9. In these sections the strength of the source is taken to be constant over its area; a brief discussion of variable strength is given in §12. One case in which the strength and velocity of the moving source vary with the time, namely the temperature flash occurring with a simple type of relaxation oscillation, is considered in §13. All these solutions are exact; in §10 the problem of one substance sliding on another is considered approximately by a method due to Blok (1937).* Some numerical calculations for this problem are given in §11.

2. *Notation and fundamental solutions.*

The notation of Carslaw's "Conduction of Heat" [Ed. 2 (1921)] will be used throughout, namely, v for temperature, K for conductivity, c for specific heat, ρ for density, $\kappa = K/\rho c$. When numerical values are used they are always in c.g.s. units.

The temperature at the point (x, y, z) at time t in an infinite solid, initially at zero temperature, due to a quantity of heat Q instantaneously liberated at the point (x', y', z') at zero time is†

$$\frac{Q\kappa}{8K(\pi\kappa t)^{3/2}} \exp\left[-\frac{(x-x')^2+(y-y')^2+(z-z')^2}{4\kappa t}\right] \quad \ldots\ldots\ldots \quad (1)$$

This we shall call the temperature due to an "instantaneous point source".

* In this important paper the sliding of a square source is considered with its application to the problem of the surface temperature of sliding metals. The discussion, however, is very condensed, the mathematical problems are not considered in detail, and there are few numerical results. The point of view also is different; the average temperatures, which are made fundamental here, are not discussed.

† Carslaw, *loc. cit.*, p. 150. His solution is for a quantity of heat $Q\rho c$ liberated at the point.

If we replace Q in (1) by Qdy', and integrate with respect to y' from $-\infty$ to ∞, we obtain the solution for an " instantaneous line source " parallel to the y-axis and through the point $(x', 0, z')$. Here Q heat units are instantaneously liberated per unit length of this line at zero time in the infinite solid. The temperature at the point (x, y, z) at time t due to this is [Carslaw, *loc. cit.*, §72]

$$\frac{Q}{4\pi Kt} \exp\left[-\frac{(x-x')^2+(z-z')^2}{4\kappa t}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The solutions for moving sources below are obtained by integration of these fundamental solutions.

3. *Problems on moving plane sources.*

The ultimate object of this paper is the calculation of the temperature in a semi-infinite solid, $z<0$, on which another body slides. We shall always take the plane of sliding as the plane $z=0$, and the sliding to be with constant* velocity V along the axis of x. We shall usually assume that heat is liberated at a constant rate of q, per unit time, per unit area, over the instantaneous surface of contact, and that there is no loss of heat from the remainder of the surface.

If the sliding body were a non-conductor, the whole of the heat would be taken up by the solid $z<0$, and the problem would be that of a uniform source of heat moving in the surface $z=0$ of this region with no loss of heat from the surface. This idealised problem can be solved exactly and the solution is given in §§4–9 ; the case in which the sliding body is of finite conductivity is then discussed approximately in §§10, 11.

The shape of the surface of contact is usually not known, but it may approximate either to a long narrow band, as in the case of cutting tools, or to a closed region of approximately constant diameter, as in the ordinary case of the sliding of one body on another. Accordingly we consider the mathematically most tractable† cases of these types, namely

(i) *The band source of length*‡ $2l$ in which heat is liberated uniformly at the rate q per unit area per unit time over an infinite strip parallel to the y-axis and of length $2l$ along the x-axis. The source moves with velocity V in the x-direction.

(ii) *The rectangular source of sides* 2l *parallel to the* x*-axis and* 2b *parallel to the* y*-axis* in which heat is liberated uniformly at the rate of q per unit time per unit area over the rectangle. The centre of the rectangle moves with velocity V along the x-axis. Numerical results will mostly be given for the square source in which $b=l$, but it is of some advantage to have the more general theory.

The temperatures due to the band and square sources are calculated in §§4, 5 ; other shapes are considered in §9.

4. *The steady temperature due to a band source of width* 2l *moving with velocity* V *in the plane* z=0 *of the semi-infinite solid* z<0 *with no loss of heat from the plane* z=0.

The band source is to be parallel to the y-axis and of length $2l$ parallel to the x-axis ; heat is liberated at the rate q per unit time, per unit area, over the area of the source. The result will be twice that for the same source moving

* There is no difficulty in considering variable velocity. Systems in which V and q vary with the time are frequently specified by the physical problem ; one such case is discussed in §13. It is possible also that q varies over the surface of contact, though it would be difficult to find the law of variation ; some cases of this type are considered in §12.

† In these cases the integrations in x and y can be performed independently.

‡ We shall always call the dimension of a source in the direction of motion its length, and that perpendicular to the direction of motion its width.

in the same way in infinite medium, since in the latter case there is no flow of heat over the plane $z=0$ and half the heat liberated will go into the region $z<0$.

We suppose that the motion has gone on infinitely long, so that steady conditions have been attained, and that at the instant considered, zero time, the centre of the band is at the origin. We calculate the temperature at this time at the point $(x,0,z)$. At time t earlier, the centre of the band was at $(-Vt)$ and by (2) the temperature at zero time at the point $(x,0,z)$ due to a line source of $2qdx'dt$ heat units per unit length, parallel to the y-axis and through the point $(x'-Vt,0,0)$ is

$$\frac{qdx'dt}{2\pi Kt}\exp\left[-\frac{(x-x'+Vt)^2+z^2}{4\varkappa t}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

To find the temperature at zero time for the band of length $2l$ which has been moving for infinite time, we integrate (3) with respect to x' from $-l$ to l, and with respect to t from 0 to ∞, and obtain

$$v=\frac{q}{2\pi K}\int_{-l}^{l}dx'\int_{o}^{\infty}\frac{dt}{t}\exp\left[-\frac{(x-x'+Vt)^2+z^2}{4\varkappa t}\right] \quad \ldots\ldots (4)$$

$$=\frac{q}{\pi K}\int_{-l}^{l}e^{-V(x-x')/2\varkappa}\,K_o\left\{\frac{V}{2\varkappa}[(x-x')^2+z^2]^{\frac{1}{2}}\right\}dx' \quad \ldots\ldots (5)$$

where $K_0(x)$ is the modified Bessel function of the second kind* of order zero.

Introducing the dimensionless quantities

$$X=\frac{Vx}{2\varkappa},\quad Y=\frac{Vy}{2\varkappa},\quad Z=\frac{Vz}{2\varkappa},\quad L=\frac{Vl}{2\varkappa} \quad \ldots\ldots\ldots\ldots\ldots (6)$$

(5) becomes

$$v=\frac{2q\varkappa}{\pi KV}\int_{X-L}^{X+L}e^{-u}K_0(Z^2+u^2)^{\frac{1}{2}}\,du \quad \ldots\ldots\ldots (7)$$

For the present only the temperature in the plane of the source, $z=0$, will be discussed, other values of z are considered in §7. Putting $Z=0$ in (7) it is seen that the temperatures in the plane of the source are given by

$$\frac{\pi KV}{2q\varkappa}v=I(X+L)-I(X-L) \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where † $$I(x)=\int_{o}^{x}e^{-u}K_0(|u|)du \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

so that $$I(-x)=-\int_{o}^{x}e^{u}K_0(|u|)du \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

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* Cf. Gray and Mathews, *Treatise on Bessel Functions* (Ed. 2, 1922), p. 21 (definition), p. 313 (tabulation). The integral required in (4) above is p. 51 (31).

† $|u|=u$ if $u>0$.
$=-u$ if $u<0$.

TABLE 1.

x	$I(x)$	x	$I(x)$	x	$I(x)$	x	$I(x)$	x	$I(x)$
−20	−10·277	−2·0	−2·750	−1·0	−1·781	0	0	1·0	0·932
−15	−8·789	−1·9	−2·665	−0·9	−1·664	0·1	0·328	1·1	0·945
−10	−7·024	−1·8	−2·578	−0·8	−1·541	0·2	0·505	1·2	0·956
−9	−6·623	−1·7	−2·489	−0·7	−1·412	0·3	0·626	1·3	0·965
−8	−6·199	−1·6	−2·397	−0·6	−1·275	0·4	0·713	1·4	0·972
−7	−5·748	−1·5	−2·302	−0·5	−1·128	0·5	0·778	1·5	0·977
−6	−5·265	−1·4	−2·205	−0·4	−0·969	0·6	0·827	1·6	0·981
−5	−4·741	−1·3	−2·105	−0·3	−0·794	0·7	0·864	1·8	0·987
−4	−4·164	−1·2	−2·001	−0·2	−0·595	0·8	0·892	2·0	0·991
−3	−3·513	−1·1	−1·893	−0·1	−0·357	0·9	0·914	∞	1·0

For small x

$$I(x) = -2\cdot303\, x \log_{10}|x| + 1\cdot116x + \ldots \quad \ldots\ldots\ldots \quad (11)$$

If x is large and negative, say $x < -10$, we have approximately

$$I(x) = -\sqrt{(2\pi|x|)} + 1\cdot003 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

In Table 1 a short table of values of $I(x)$ is given ; (11) and (12) will be seen to give adequate approximations in the relevant regions.

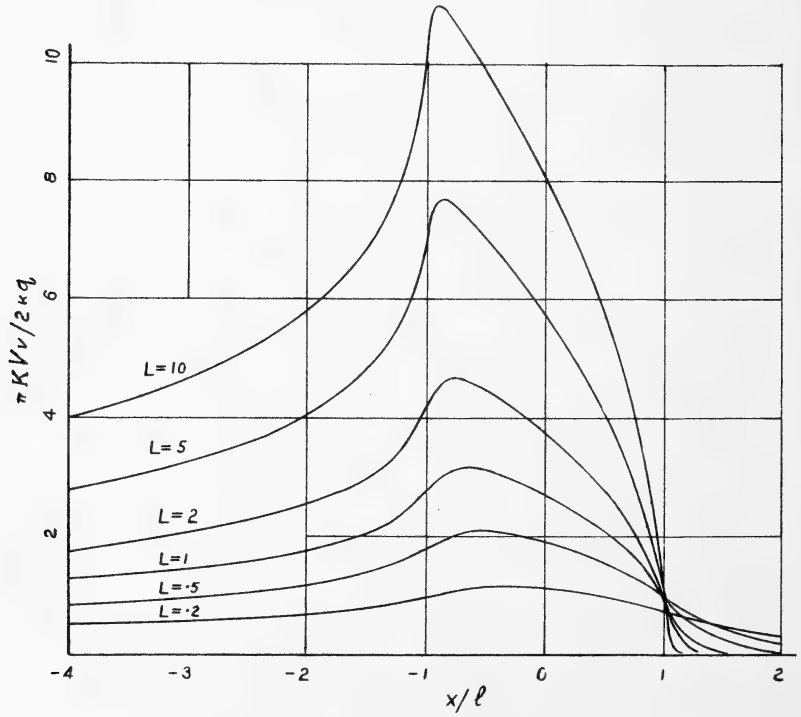

Fig. 1.

In Fig. 1 the values of $(\pi KV/2q\varkappa)v$, which give the temperature variation in the plane of the moving source, are plotted, for various values of L, in terms of the ratio

$$\xi = X/L = x/l.$$

These vary from the symmetrical form for very small L, given, for small X, by

$$\frac{\pi KV}{2q\kappa}v = -2\cdot303(X+L)\log_{10}|X+L| + 2\cdot303(X-L)\log_{10}|X-L| + 2\cdot232\,L \quad \ldots\ldots\ldots \quad (13)$$

to the form for large L, given, approximately, by

$$\left.\begin{aligned}\frac{\pi KV}{2q\kappa}v &= \{2\pi(L-X)\}^{\frac{1}{2}} \qquad , \quad -L<X<L \\ &= (2\pi)^{\frac{1}{2}}\{(L-X)^{\frac{1}{2}} - (|X+L|)^{\frac{1}{2}}\}, \quad X<-L\end{aligned}\right\} \quad \ldots\ldots \quad (14)$$

this has a maximum at the rear end of the source, $X=-L$.

For intermediate values of L the curves show a maximum at some point between the centre and the rear of the source, which moves progressively towards the rear as L increases.

5. *The steady temperature for a rectangular source of sides* 2l *and* 2b, *parallel to the* x *and* y *axes respectively, whose centre moves with velocity* V *along the* x*-axis in the plane* z=0 *of semi-infinite solid* z<0 *with no loss of heat from the plane* z=0.

Here, by the method of §4, using (1) in place of (2), we obtain for the temperature at the point (x,y,z), when the centre of the source is at the origin,

$$\frac{\kappa q}{\pi KV}\int_{X-L}^{X+L} e^{-\eta}\,d\eta \int_{Y-B}^{Y+B} \frac{\exp\{-(\eta^2+\zeta^2+Z^2)^{\frac{1}{2}}\}}{(\eta^2+\zeta^2+Z^2)^{\frac{1}{2}}}d\zeta \quad \ldots\ldots \quad (15)$$

where the notation (6) has been used, and $bV/2\kappa=B$. In the plane $z=0$ there is now a temperature variation in y as well as in x; the temperature is greatest at points on the x-axis. Here, putting $Y=Z=0$ in (15), we have

$$\frac{\pi KV}{2\kappa q}v = \int_{X-L}^{X+L} e^{-\eta}d\eta \int_{o}^{B} \frac{e^{-(\eta^2+\zeta^2)^{\frac{1}{2}}}}{(\eta^2+\zeta^2)^{\frac{1}{2}}}d\zeta \quad \ldots\ldots\ldots\ldots \quad (16)$$

$$= \int_{X-L}^{X+L} e^{-\eta}K_0(|\eta|)d\eta - \int_{X-L}^{X+L} e^{-\eta}d\eta \int_{B}^{\infty} \frac{e^{-(\eta^2+\zeta^2)^{\frac{1}{2}}}}{(\eta^2+\zeta^2)^{\frac{1}{2}}}d\zeta \quad \ldots\ldots\ldots\ldots\ldots \quad (17)$$

For large B the result (17) tends to that for the band source, (7), and for moderate values the difference is small.

For small values of L, X and B we may replace the exponentials in (16) by unity and obtain approximately

$$\frac{\pi KV}{2\kappa q}v = (X+L)\log_e\frac{B+[(X+L)^2+B^2]^{\frac{1}{2}}}{X+L} + B\log_e\frac{X+L+[(X+L)^2+B^2]^{\frac{1}{2}}}{B} + (L-X)\log_e\frac{B+[(L-X)^2+B^2]^{\frac{1}{2}}}{L-X} + B\log_e\frac{L-X+[(L-X)^2+B^2]^{\frac{1}{2}}}{B} \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

for the most important case $-L<X<L$, with similar expressions for the other regions in X.

The temperatures for a square source at points on the x-axis are shown in Fig. 2, where $(\pi KVv/2q\kappa)$, given by (16), is plotted against $\xi=X/L=x/l$. Curves I, III and V are for $L=0\cdot2$, 1 and 2, respectively, while curves II, IV and VI are the corresponding ones for the band source. It is seen that even for values

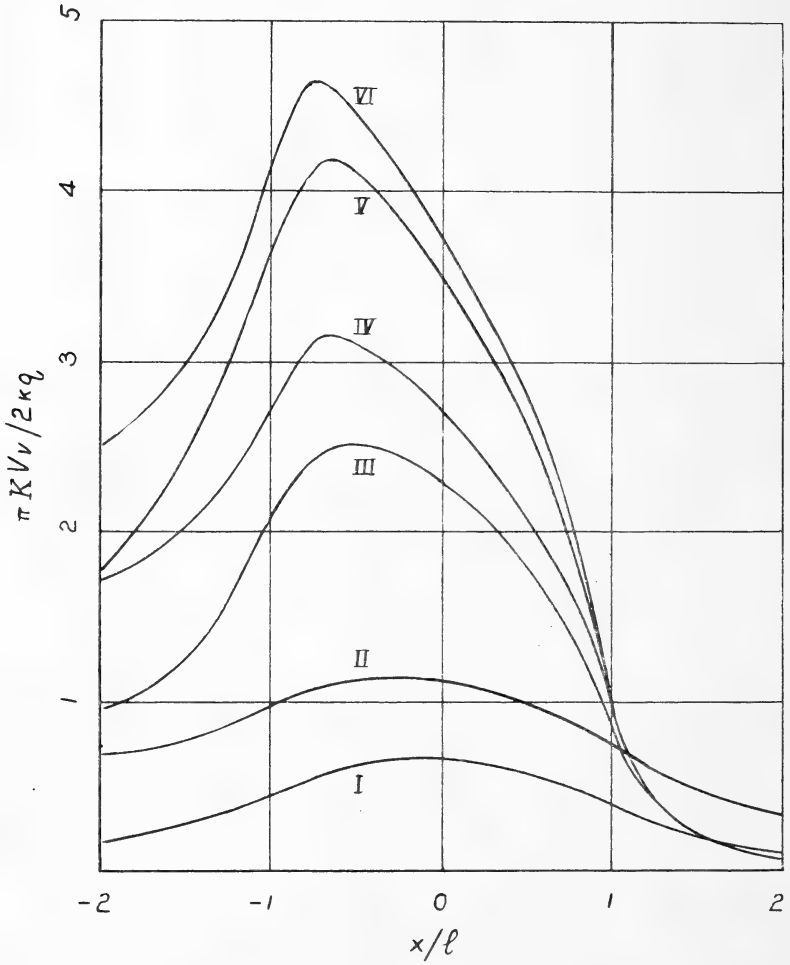

Fig. 2.

of L as small as 1 the difference between the temperatures for square and band sources of the same L is small; for much smaller values of L the difference is important, but then simple approximation formulæ are available. The question is further discussed in §9, where the maximum and average temperatures for band and square sources are given.

Since for this problem when $L>1$ the behaviour of band and square sources is so similar, it follows that when discussing more complicated problems such as those of §§7, 12, 13 it is sufficient, if L is not too small, to treat those for the band source, for which calculations are usually much easier, and the results for the square source may be expected not to be very different.

6. *The case in which motion of the source has taken place for a finite time* T.

We consider a rectangular source with sides $2l$ parallel to the x-axis and $2b$ parallel to the y-axis. Its centre moves with velocity V along the x-axis in the plane $z=0$ in semi-infinite medium $z<0$ with no loss of heat from the plane $z=0$. Suppose that at time T the centre of the source has just reached the origin. It follows from (1) that the temperature at time T at the point (x,y,z) is

$$\frac{q\kappa}{4(\pi\kappa)^{3/2}K}\int_o^T \frac{dt}{(T-t)^{3/2}}\int_{-l}^{l} dx'\int_{-b}^{b} dy'$$

$$\exp\left[-\frac{[(x-x'+V(T-t)]^2+(y-y')^2+z^2}{4\kappa(T-t)}\right]$$

$$=\frac{q\kappa}{2KV(2\pi)^{\frac{1}{2}}}\int_o^{V^2T/2\kappa}\frac{du}{u^{\frac{1}{2}}}e^{-Z^2/2u}\left\{\operatorname{erf}\frac{Y+B}{(2u)^{\frac{1}{2}}}-\operatorname{erf}\frac{Y-B}{(2u)^{\frac{1}{2}}}\right\}$$

$$\times\left\{\operatorname{erf}\frac{X+L+u}{(2u)^{\frac{1}{2}}}-\operatorname{erf}\frac{X-L+u}{(2u)^{\frac{1}{2}}}\right\} \quad \ldots\ldots (19)$$

where, as before,

$$X=\frac{Vx}{2\kappa},\ Y=\frac{Vy}{2\kappa},\ Z=\frac{Vz}{2\kappa},\ L=\frac{Vl}{2\kappa},\ B=\frac{Vb}{2\kappa} \quad \ldots\ldots\ldots\ldots\ldots\ldots (20)$$

and

$$\operatorname{erf} x=\frac{2}{\sqrt{\pi}}\int_o^x e^{-u^2}du \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

so that erf $\infty=1$.

Letting $B=\infty$ in (19) we find for the band source

$$\frac{\pi KV}{2q\kappa}v=\tfrac{1}{2}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\int_o^{V^2T/2\kappa} e^{-Z^2/2u}\left\{\operatorname{erf}\frac{X+L+u}{(2u)^{\frac{1}{2}}}-\operatorname{erf}\frac{X-L+u}{(2u)^{\frac{1}{2}}}\right\}\frac{du}{u^{\frac{1}{2}}} \quad \ldots\ldots (22)$$

and if $T=\infty$ in this we obtain an alternative form of (7).

For points on the x-axis, we put $Y=Z=0$ in (19). This gives

$$\frac{\pi KV}{2q\kappa}v=\tfrac{1}{2}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\int_o^{V^2T/2\kappa}\frac{du}{u^{\frac{1}{2}}}\left\{\operatorname{erf}\frac{X+L+u}{(2u)^{\frac{1}{2}}}-\operatorname{erf}\frac{X-L+u}{(2u)^{\frac{1}{2}}}\right\}\operatorname{erf}\frac{B}{(2u)^{\frac{1}{2}}}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (23)$$

and if $T=\infty$ in this we obtain an alternative form of (17) which is sometimes convenient.

We may also obtain from (19) a convenient form for the average temperature over the area of the source

$$v_{\mathrm{av}}=\frac{1}{4BL}\int_{-L}^{L}dX\int_{-B}^{B}vdY \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (24)$$

It is given by

$$\frac{\pi KV}{2q\kappa}v_{\mathrm{av}}=\frac{1}{4LB}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\int_0^{V^2T/2\kappa}u^{\frac{1}{2}}du\Phi(B(2/u)^{\frac{1}{2}})\times\left\{\Phi\left(\frac{2L+u}{(2u)^{\frac{1}{2}}}\right)+\Phi\left(\frac{|2L-u|}{(2u)^{\frac{1}{2}}}\right)-2\Phi[(u/2)^{\frac{1}{2}}]\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots (25)$$

where $\Phi(x)=\int_0^x \mathrm{erf}\ x\ dx$

$$=x\ \mathrm{erf}\ x-\frac{1}{\pi^{\frac{1}{2}}}+\frac{1}{\pi^{\frac{1}{2}}}\ e^{-x^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (26)$$

Letting $B\to\infty$ in (25) we obtain the corresponding result for a band source

$$\frac{\pi KV}{2q\kappa}v_{\mathrm{av}}=\frac{\pi^{\frac{1}{2}}}{4L}\int_0^{V^2T/2\kappa}\left\{\Phi\left(\frac{2L+u}{(2u)^{\frac{1}{2}}}\right)+\Phi\left(\frac{|2L-u|}{(2u)^{\frac{1}{2}}}\right)-2\Phi[(u/2)^{\frac{1}{2}}]\right\}du \quad \ldots\ldots\ldots\ldots\ldots\ldots (27)$$

As an illustration of the way in which the temperatures build up to the final values given in §§4, 5 the temperatures at the centre, $X=Y=Z=0$, of a square source, $B=L$, calculated from (19) are shown in Fig. 3. $(\pi KVv/2q\kappa)$ is plotted against $V^2T/2\kappa$ for the values 0·2, 0·5, 1, 2, 5 of L. In Fig. 4 the time T' to reach half the final value is shown, $V^2T'/2\kappa$ being plotted against L.

7. *Penetration perpendicular to the plane of the source.*

The most important quantities for practical applications are the temperatures in the plane of the source, $z=0$, but the temperatures for other values of z are easily obtained from (7) or (22) for the band source, and from (15) or (19) for the square source. Only those for the band source will be discussed here since they are easier to calculate and contain all the essential features ; the temperatures for the square source are of course lower.

In Fig. 5 curves of $(\pi KV/2q\kappa)v$ plotted against $\xi=X/L=x/l$ are given for a band source of length $L=1$ for the values 0, 0·2, 0·5, 1, 2, 4 of Z. The maxima of the curves are seen to move steadily to the left as Z increases ; this effect is caused by diffusion of heat from the surface inwards after the source has passed.

To show how the temperature varies with Z for different values of the length of the source, $(\pi KV/2q\kappa)v$ at the rear end of the source, $X=-L$, is plotted against Z in Fig. 6 for the values 0·2, 0·5, 1, 2, 4 of L. As a numerical example we consider the case discussed in §11, Table III, $l=0\cdot001$ cm., $V=700$ cm./sec., $\kappa=0\cdot173$, so that $L=2$. Here it follows from Fig. 6 that the temperature in the medium below the rear end of the source has fallen to 1/10 of its surface value when $Z=3$, i.e. at a depth of 0·0015 cm. Thus in most cases the penetration into the medium is extremely shallow, and from this several results of practical importance follow : (i) the thermal stresses due to these fluctuating temperatures will be very superficial, (ii) a change in thermal properties of a thin layer on the surface may make a large change in the surface temperature.* If the con-

* This remark applies in moving sources and not to the stationary sources of §8 for which the penetration, given by (28), is deeper.

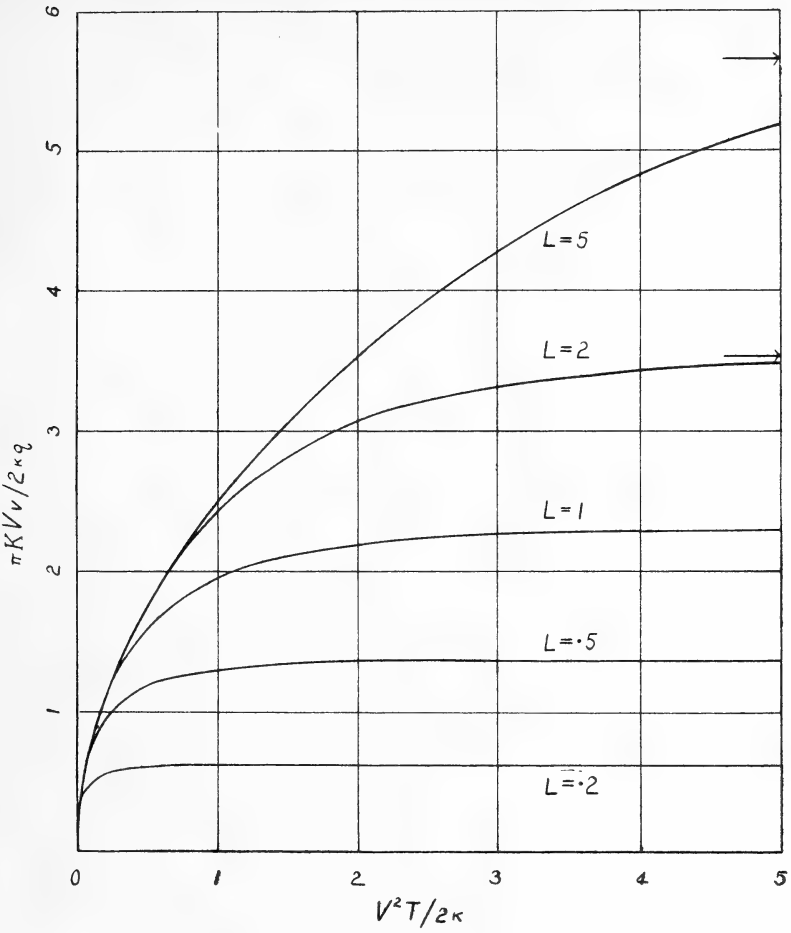

Fig. 3.

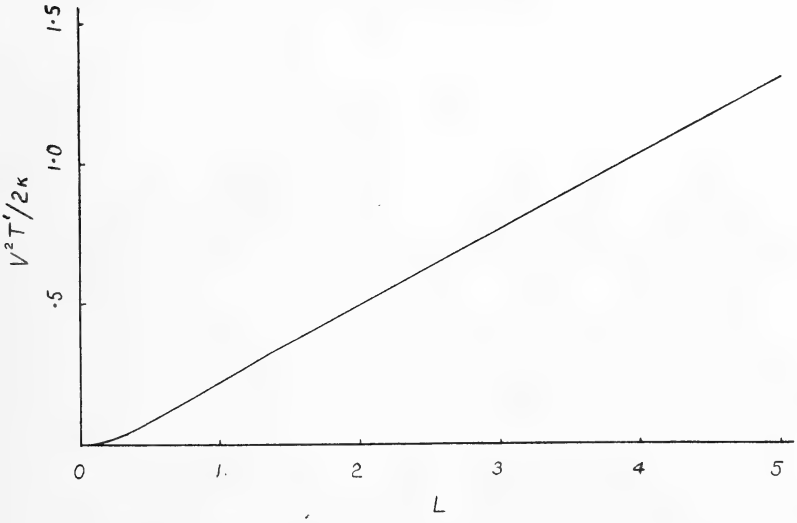

Fig. 4.

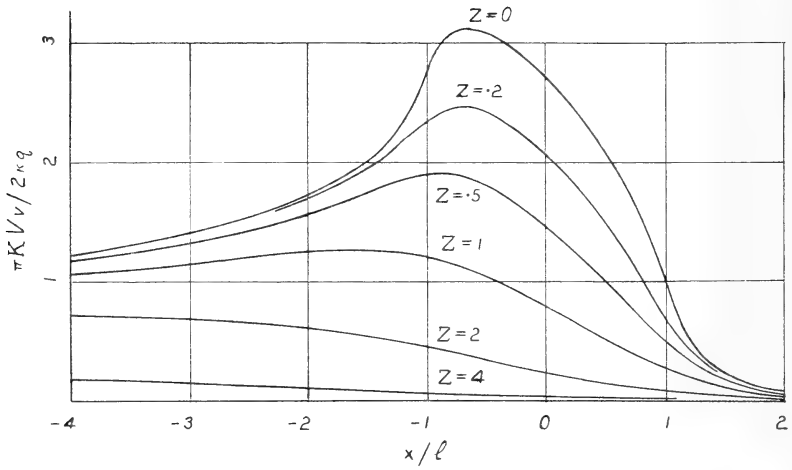
Z=0
Z=·2
Z=·5
Z=1
Z=2
Z=4
πKVv/2κq
x/ℓ
-4
-3
-2
-1
0
1
2
1
2
3

Fig. 5.

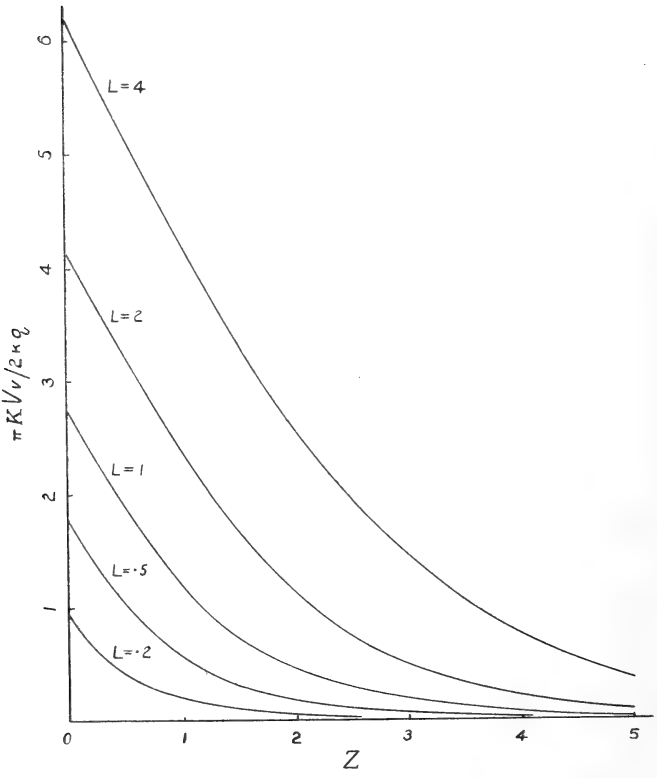
L=4
L=2
L=1
L=·5
L=·2
πKVv/2κq
Z
0
1
2
3
4
5
1
2
3
4
5
6

Fig. 6.

ductivity of the surface layer is raised, for example by applying a thin coating of a good conductor, the surface temperature will be lowered; while if the conductivity of the surface layer is lowered, the surface temperature will be raised.

At the same time it should be remarked that, although the penetration is small, it is fairly large on a molecular scale, and thus estimates of surface temperature based on the heating of monolayers will not be satisfactory.

8. *Stationary sources.*

The temperature at time t, at the point (x,y,z), in the semi-infinite solid $z<0$ with no flow of heat over the surface $z=0$, due to heat supplied at the rate q per unit time per unit area over the square $-l<x'<l$, $-l<y'<l$, $z'=0$, commencing at zero time, when the solid is at zero temperature, is

$$\frac{q\kappa}{4K(\pi\kappa)^{3/2}}\int_0^t \frac{dt'}{(t-t')^{3/2}}\int_{-l}^{l} dx'\int_{-l}^{l} dy'\exp\left[-\frac{(x-x')^2+(y-y')^2+z^2}{4\kappa(t-t')}\right].$$

To find the steady state temperature we put $t=\infty$ in this and obtain

$$\frac{q}{2K\pi}\int_{-l}^{l} dx'\int_{-l}^{l} dy'\{(x-x')^2+(y-y')^2+z^2\}^{-\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

The maximum temperature occurs at $x=y=z=0$ and is*

$$\frac{4lq}{K\pi}\log_e(1+\sqrt{2})=1\cdot122\ \frac{lq}{K} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

The average temperature over the area of the source is

$$\frac{4lq}{K\pi}\left\{\log_e(1+\sqrt{2})-\frac{\sqrt{2}-1}{3}\right\}=0\cdot946\ \frac{lq}{K} \quad \ldots\ldots\ldots\ldots\ldots \quad (30)$$

The corresponding result for the maximum temperature for a circular source of radius l is

$$ql/K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

One further result of this type will be needed subsequently, namely, the temperature in a semi-infinite square† rod of side $2l$ which radiates heat from its faces with emissivity σ. There is a source of strength q per unit time per unit area over the end and no loss of heat from the end. Then, when the source has been established for a sufficient time for steady state conditions to be attained, the temperature in the source plane is (treating the problem as one-dimensional)

$$q\left(\frac{l}{2K\sigma}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (32)$$

9. *The maximum and average steady temperatures over the area of the source.*

These are the most important quantities for physical applications and are collected here for reference. In experiments in which temperatures are measured by using two sliding metals as a thermocouple it is the average temperatures which are measured.

* In Blok, (1937) (8), there is a misprint of 200 for 2. The exact value is $4\pi^{-\frac{1}{2}}\log_e(1+\sqrt{2})=1\cdot989$.

† This is the model of Bowden and Ridler (1936), except that a square rod is used here in place of their round one. This paper will be referred to as B.R.

From the results of §4 it follows that for a band source

(i) If L is large, say $L>5$, the maximum temperature is (using (14))

$$\frac{4q\kappa L^{\frac{1}{2}}}{KV\pi^{\frac{1}{2}}}=\frac{2q}{K}\left(\frac{2\kappa l}{\pi V}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (33)$$

and the average temperature over the area of the source is

$$\frac{8q\kappa L^{\frac{1}{2}}}{3KV\pi^{\frac{1}{2}}}=\frac{1\cdot 064q}{K}\left(\frac{\kappa l}{V}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (34)$$

(ii) If L is small, say $L<0\cdot 1$, the maximum temperature is (using (13))

$$\frac{4q\kappa}{\pi KV}\{-2\cdot 303L\ \log_{10} L+1\cdot 116L\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (35)$$

and the average temperature is

$$\frac{4q\kappa}{\pi KV}\{-2\cdot 303L\ \log_{10} 2L+1\cdot 616L\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (36)$$

For the square source we have from the results of §5 :

(i) If L is large, the maximum and average temperatures are nearly the same as those for a band source, namely, (33) and (34).

(ii) If L is small, the maximum temperature is, from (18)

$$\frac{8q\kappa L}{\pi KV}\log_e (1+\sqrt{2})=1\cdot 122\ \frac{ql}{K} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (37)$$

and the average temperature over the area of the source is

$$\frac{8\kappa qL}{\pi KV}\left\{\log_e (1+\sqrt{2})-\frac{\sqrt{2}-1}{3}\right\}=0\cdot 946\ \frac{ql}{K} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (38)$$

For intermediate values, i.e. $0\cdot 1<L<5$, where the above formulæ do not hold, the maximum temperatures must be obtained from curves such as those of Figs. 1 and 2 and the average temperatures are most easily calculated from (25) and (27). These results are given in Fig. 7 where $(\pi KV/2\kappa q)$ times the maximum and average temperatures for band and square sources are plotted against L. Curves I and II are the maximum temperatures for the band and square sources respectively, while curves III and IV are average temperatures for band and square sources.

It can now be seen that the temperatures (and in particular the average temperatures of Fig. 7) for the square source may be used for any not too irregular shape of source. Several cases may arise : (i) If $L>2$ the difference between the band and square source solutions is small, it follows that for lengths of this order elongation of the source perpendicular to the direction of motion does not affect the result. (ii) For very small L the results for the band and square sources do differ, the former behaving like $L\log L$ and the latter like L. (iii) For very small L the results for the moving source tend to those for a stationary source of the same size and strength, this was pointed out by Blok (*loc. cit.*) ; for example, (37) and (38) for the moving square source with small L are identical with (29) and (30) for the stationary square source. This result enables us to compare the results for shapes other than rectangular ; for example, (29) for the maximum temperature in a square source of side $2l$, and (31) for a circular source of diameter $2l$ differ by 12%, so that such a change of shape of the source which does not affect the length in the direction of motion may be expected not to affect the temperature materially. (iv) There remains the possibility of a source elongated in the direction of motion ; an increase of L for constant B will give a large increase of temperature which may be calculated from the rectangular source formulæ, but the question of the greatest practical interest

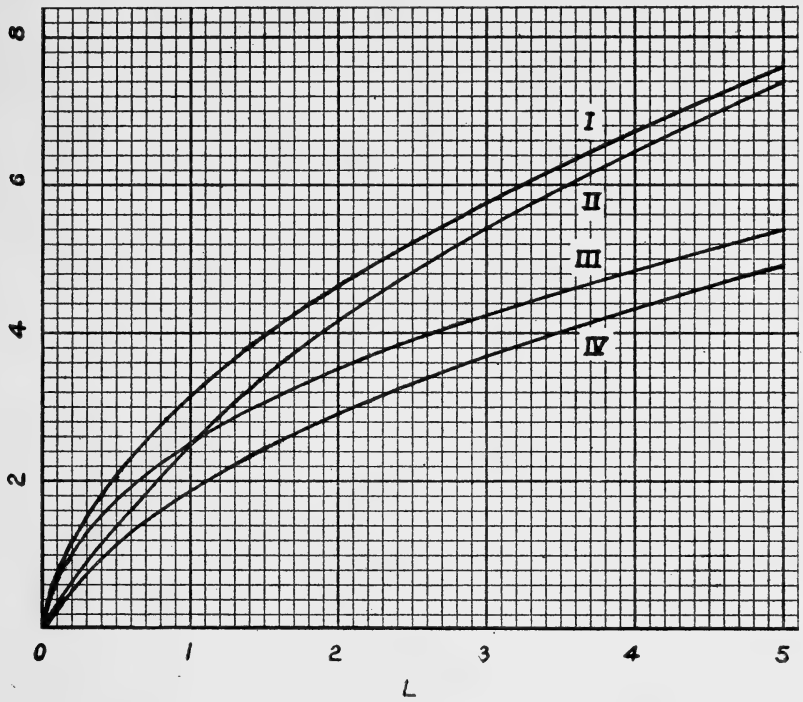

Fig. 7.

in this and the other cases is the way in which the average temperature over the area of the source varies when the shape of the source varies but its area remains constant. This is most easily studied by considering rectangular sources with constant LB : in Table II average temperatures are given for the case $LB=1$.

Table 2.

L.	B.	$(\pi KV/2\varkappa q)v_{av}$.
5	0·2	1·243
2	0·5	1·792
1	1	1·879
0·5	2	1·580
0·2	5	0·994

It is seen that increasing the width B of the source at the expense of the length L lowers the average temperatures, which for large widths tend to those for a band source. Increasing the length at the expense of the width also lowers the average temperature, but to a rather less degree. The most interesting point which emerges from Table II is that for the wide range of shapes considered there, the average temperatures differ by a factor of less than two.

Finally it may be remarked that the curves of Fig. 7 show the relative orders of magnitude of the average and maximum temperatures ; thus if the average temperature is known (e.g. experimentally) the maximum temperature can be inferred.

10. *Application to the surface temperature of sliding solids.*

The practical problem arising in connection with the generation of heat by friction is the following : one substance, which we shall call the slider, of thermal properties K_2, $\varkappa_2$, slides with velocity V over the surface of a second substance, K_1, $\varkappa_1$, which is at rest.

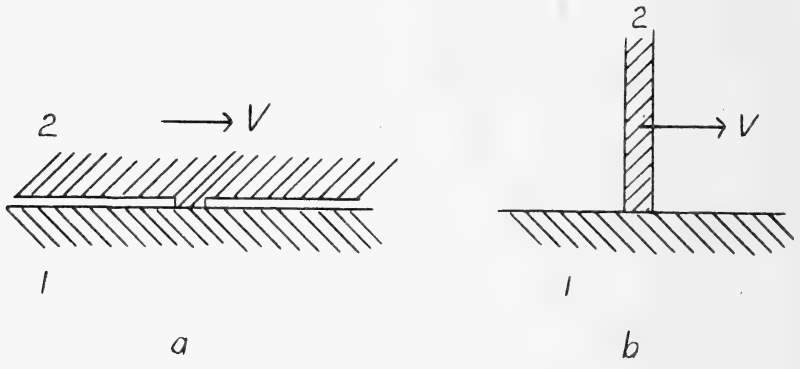

Fig. 8.

We shall discuss two types of slider, represented by Fig. 8, (*a*) and (*b*). In the former a protuberance of the semi-infinite substance 2 slides on the semi-infinite substance 1 ; this is the case normally encountered, the latter case of a long thin slider has been discussed by Bowden and Ridler (*loc. cit.*), who have used it to discuss their experimental results.

We may reasonably assume that heat is generated at a uniform rate per unit time per unit area over the common surface, and that there is no loss of heat from the portions of the surfaces not in contact, so that the model of the preceding sections in which a source moves in the surface of a semi-infinite medium provides a first approximation. If the substance 2 were a perfect insulator the moving source theory of §§3-7 would be exactly applicable in the medium 1 ; likewise if the substance 1 were a perfect insulator the stationary source theory of §8 would be exactly applicable in the medium 2. The practical case in which both bodies have finite conductivity is much more difficult, the slider is *heated* by the source and *cooled* by the oncoming cooler portions of substance 1, while the substance 1 is heated both by the source and by conduction from the slider. An exact discussion seems to be out of the question* at present so we use the following approximate method.† We assume that when a steady state‡ has been attained a fraction α of the heat q per unit time per unit area generated over the area of contact passes to the substance 1 and the remaining fraction $(1-\alpha)$ to the substance 2. α then will be calculated by the requirement that the average temperature over the area of contact calculated by §9 for a moving source αq in substance 1 equals the average temperature calculated for substance 2 by §8 with a stationary source $(1-\alpha)q$. Any method of this sort

* It is possible to give an exact treatment of particular models, but these are very cumbersome and add nothing to the general conclusions.

† Due to Blok, *loc. cit.* He uses it first for a stationary source at a junction of two media of different conductivities and then applies it to the problem of a moving slider, using a different criterion to that developed here. It should be remarked that even for a stationary source the method is only strictly accurate after infinite time when steady state conditions have been attained : for finite time the heat will divide between the two media in a different ratio, for example an instantaneous infinite plane source at the junction divides in the ratio $K_1\varkappa_2^{\frac{1}{2}}/K_2\varkappa_1^{\frac{1}{2}}$, in place of K_1/K_2.

‡ This assumes that motion has gone on for a time of the order of those in §6, Fig. 4.

will necessarily be approximate since the two temperature distributions over the area of contact calculated in this way will be different, thus any reasonable criterion for calculating α may be used ; that of equating average temperatures used here has been chosen because the average temperature is the quantity experimentally observed, and also because it is easily calculated and the single quantity best representative of the temperature distribution. α of course will depend both on the velocity, the area of contact, and the thermal constants of the two substances. Bowden and Ridler, *loc. cit.*, consider the slider only and take α to be a constant, so their discussion is not satisfactory.

We now calculate the average surface temperatures on the above assumptions.

Case (i). A semi-infinite slider K_2, κ_2, with a square contact of sides $2l$ moving with velocity V on a semi-infinite medium K_1, κ_1 [cf. Fig. 8 (*a*)]. We suppose a fraction α of the heat q generated per unit time per unit area to go to the medium and $(1-\alpha)$ to the slider.

If $L=Vl/2\kappa_1$ is small, equating the average temperatures over the area of contact given by (38) and (30) we have

$$0\cdot946\frac{\alpha ql}{K_1}=0\cdot946\frac{(1-\alpha)ql}{K_2}.$$

Thus $$\alpha=\frac{K_1}{K_1+K_2} \quad \ldots\ldots (39)$$

and the average temperature is $$0\cdot946\frac{ql}{K_1+K_2} \quad \ldots\ldots (40)$$

For the case in which L is large, comparing (34) and (30) we have

$$1\cdot064\frac{\alpha q}{K_1}\left(\frac{\kappa_1 l}{V}\right)^{\frac{1}{2}}=0\cdot946\frac{(1-\alpha)ql}{K_2}.$$

Thus $$\alpha=\frac{K_1(lV)^{\frac{1}{2}}}{1\cdot125K_2\kappa_1^{\frac{1}{2}}+K_1(lV)^{\frac{1}{2}}} \quad \ldots\ldots (41)$$

and the average temperature over the area of contact is

$$\frac{1\cdot064\ ql\kappa_1^{\frac{1}{2}}}{1\cdot125\ K_2\kappa_1^{\frac{1}{2}}+K_1(lV)^{\frac{1}{2}}} \quad \ldots\ldots (42)$$

If V is large enough for the first term of the denominators of (41) and (42) to be neglected, we have $\alpha=1$ and (42) reduces to (34) ; no heat is taken by the slider and the surface temperature is that due to a source q moving in the medium 1 with no loss of heat over the plane $z=0$.

For intermediate values of L the average temperatures for the substance 1 must be obtained from Fig. 7, curve IV. If $y=(\pi K_1V/2\alpha q\kappa_1)v_{\mathrm{av}}$ is the ordinate of this curve for abscissa L we find, equating this value to that obtained from (30)

$$\alpha=\frac{1\cdot486\ lK_1V}{1\cdot486\ lK_1V+\kappa_1K_2y} \quad \ldots\ldots (43)$$

and the average temperature is

$$\frac{0\cdot946\ l\kappa_1yq}{1\cdot486\ lK_1V+\kappa_1K_2y} \quad \ldots\ldots (44)$$

Case (ii). A long square slider of side $2l$, with thermal constants K_2, κ_2 and emissivity σ from its sides, slides with velocity V on a semi-infinite medium K_1, κ_1 [cf. Fig. 8 (*b*)]. If, as before, we suppose a fraction α of the heat generated to go to the medium 1, comparing average surface temperatures (38) and (32) gives, for the case of L small,

$$0\cdot946\ \frac{\alpha ql}{K_1}=(1-\alpha)\ \frac{ql^{\frac{1}{2}}}{(2K_2\sigma)^{\frac{1}{2}}}$$

Thus $$\alpha=\frac{K_1}{K_1+1\cdot338(lK_2\sigma)^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (45)$$

and the mean temperature over the area of contact is

$$\frac{0\cdot946\ ql}{K_1+1\cdot338(lK_2\sigma)^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (46)$$

If L is large, using (34) and (32), we find

$$\alpha=\frac{K_1V^{\frac{1}{2}}}{K_1V^{\frac{1}{2}}+1\cdot504(\varkappa_1K_2\sigma)^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (47)$$

and for the average temperature

$$\frac{1\cdot064\ q(\varkappa_1l)^{\frac{1}{2}}}{K_1V^{\frac{1}{2}}+1\cdot504(\varkappa_1K_2\sigma)^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (48)$$

Here, as in Case (i), if V is large, $\alpha\rightarrow1$ and the average temperature to (34).

For intermediate values of L we use (32) and the results of Fig. 7.

11. *Numerical calculations of particular cases.*

Any attempt to calculate temperatures on the above basis requires a knowledge of q, and this requires a knowledge of the size and number of the points of contact. For this reason we consider only the case of a single contact which we shall take to be a square of side $2l$. Then if the load on the slider is W gm., the coefficient of friction μ, and J the mechanical equivalent of heat

$$q=\frac{\mu WgV}{4l^2J} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (49)$$

We consider first the model of Fig. 8 (*a*), §10, Case (i); inserting (49) in the results (40) and (42) we find for the average temperature over the area of contact, if $L=lV/2\varkappa_1$ is small,

$$\frac{0\cdot236\ \mu WgV}{lJ(K_1+K_2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (50)$$

and if L is large the result is

$$\frac{0\cdot266\ \varkappa_1^{\frac{1}{2}}\mu WgV}{lJ(1\cdot125\ K_2\varkappa_1^{\frac{1}{2}}+K_1(lV)^{\frac{1}{2}})} \quad \ldots\ldots\ldots\ldots\ldots \quad (51)$$

If the area of contact remains fixed the temperatures attained are thus proportional to the velocity when L is small, and to the square root of the velocity for large L. For intermediate values of L a transition curve given by (44) and (49) is obtained. This is best illustated by a numerical example involving this range. We consider mild steel sliding on mild steel with $K_1=K_2=0\cdot144$, $\varkappa_1=\varkappa_2=0\cdot173$, $W=400$, $\mu=0\cdot23$, $l=10^{-3}$. The results are shown in Table III, where the values of L, α defined as in §10, and the average temperature v_{av} are given for various values of V.

TABLE 3.

V.	L.	α.	v_{av}.
			° C.
1,500	4·34	0·74	1,370
1,000	2·89	0·70	1,040
700	2·02	0·67	810
500	1·45	0·64	630
200	0·578	0·58	300
100	0·289	0·54	160
70	0·202	0·53	115
50	0·145	0·52	85
20	0·058	0·51	35

It will be seen that α tends to $\frac{1}{2}$ for small values of V, and increases steadily as V increases. Also the curve of v_{av} against V shows a slight curvature over all but the early part of its length, say for $V>200$, i.e., $L>0\cdot5$. The experimental curves of temperature against velocity in B.R. are linear for temperatures not too close to the melting point, this indicates that small values of L must be in question, say $L<0\cdot5$. For example the curves, B.R. Fig. 6 (*a*), for constantan on mild steel are linear up to $V=1{,}000$, and the criterion $L<0\cdot5$ implies for this case $l<1\cdot7\times10^{-4}$ cm. The temperature calculated from (44) and (49) for constantan on mild steel with $V=1{,}000$, $l=1\cdot7\times10^{-4}$, is 3,140° C. as against 940° C. experimentally. Thus the criterion $L<0\cdot5$ is perhaps too restrictive; if we take $l=4\cdot5\times10^{-4}$, which gives theoretically 940° C. at $V=1{,}000$, the curve of temperature against velocity has a slight curvature, for example its value at $V=500$ is 560° C. as against 470° C. experimentally. It appears that fairly good agreement between theory and experiment can be obtained in this rather extreme case provided l is taken to be small; in most cases l will be small and V moderate, so that L will be small, the temperature curves will be linear, and (50) may be regarded as the most suitable simple formula for comparison with experiment.

We now consider the model of Fig. 8 (*b*) and §10, Case (ii); this has the considerable disadvantage that $4l^2$ enters both as the area of the slider and the area of contact; in practice, even with a narrow slider, the area of contact will be much less than the area of the slider and the problem will approximate to that of Fig. 8 (*a*). It seems worth while discussing the model briefly on account of its use in B.R.

Introducing (49) in (46) and (48), the average temperature over the area of contact for small L is found to be

$$\frac{0\cdot236\ \mu WgV}{lJ(K_1+1\cdot338(lK_2\sigma)^{\frac{1}{2}})} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (52)$$

and for large L

$$\frac{0\cdot266\ \mu WgV\varkappa_1^{\frac{1}{2}}}{Jl^{3/2}(K_1V^{\frac{1}{2}}+1\cdot504(\varkappa_1K_2\sigma)^{\frac{1}{2}})} \quad \ldots\ldots\ldots\ldots\ldots \quad (53)$$

(52) and (53) are free from the objectionable features* of the formula [B.R. (5), π is replaced by 4 to correspond to a square slider, and α by $1-\alpha$ to correspond with the present notation]

$$\frac{(1-\alpha)\mu WgV}{4Jl(2\sigma K_2l)^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (54)$$

which, if α is taken to be constant as in B.R., makes the temperature tend to infinity as $\sigma\to0$, or as $K_2\to0$.

In Table IV calculated average temperatures for several values of l are given for the case considered in B.R. [Table I, p. 643] of a constantan slider, $K_2=0\cdot055$, $\sigma=0\cdot00095$, sliding on a mild steel surface, $K_1=0\cdot144$, $\varkappa_1=0\cdot173$, with $V=100$, $W=100$, $\mu=0\cdot23$. The three columns give the result calculated from (54) with $\alpha=\frac{1}{2}$, that calculated as in §10, Case (ii), and that calculated as in §10, Case (i), for constantan on mild steel.

It will be seen that (54) with $\alpha=\frac{1}{2}$ indicates results which are far too high, since the value of α in all cases is in fact almost 1. The conclusion seems to be that, though high temperatures can be obtained theoretically, they require much smaller areas of contact than those indicated in B.R., Table I.

* The formula (54) has been criticised by Morgan, Muskat and Reed (1941), on the ground that it makes the temperature tend to infinity as $l\to0$. This, however, is simply a consequence of the assumption (49) that a finite quantity of heat $\mu WgV/J$ per unit time is liberated at the source; if the area of the source tends to zero we have a point source of finite strength which gives infinite temperature at the point.

Table 4.

l	(54)	Case (ii).	Case (i).
cm.	° C.	° C.	° C.
0·05	59	0·4	0·3
0·0158	332	1·9	1·7
0·005	1,860	9·8	8·1
0·001	20,770	75·0	57·0
0·0005	59,000	164·0	120·0
0·0001		880·0	640·0

Finally the way in which, other things being equal, the average temperatures vary with the conductivities of the two substances may be considered. It has been remarked above that (50) is the simplest formula likely to give reasonable agreement with experimental results. This gives a temperature proportional to

$$\frac{1}{K_1+K_2}$$

while (54) gives a temperature variation with $K_2^{-\frac{1}{2}}$, and rather better agreement with experiment.* The way in which the temperatures vary can be seen from Table V, which shows $\frac{1}{K_1+K_2}$ and $K_2^{-\frac{1}{2}}$ for various combinations.

Table 5.

Substance 2.	Substance 1.	K_2.	K_1.	$\frac{1}{K_1+K_2}$	$K_2^{-\frac{1}{2}}$.
Copper	Mild steel ..	0·918	0·144	0·94	1·04
Mild steel	Mild steel ..	0·144	0·144	3·47	2·63
Lead	Mild steel ..	0·0827	0·144	4·41	3·48
Bismuth	Mild steel ..	0·0194	0·144	6·12	7·18
Copper	Copper ..	0·918	0·918	0·54	1·04
Glass	Copper ..	0·0017	0·918	1·09	24·0
Silk	Copper ..	0·0001	0·918	1·09	100·0
Silk	Glass	0·0001	0·0017	550·0	100·0

It is seen that for ordinary values of the conductivity, with the $1/(K_1+K_2)$ law a fairly large variation in average temperature can be obtained by varying the conductivity of one of the substances, but extremely high values of the temperature cannot be obtained unless both substances are of very low conductivity.

12. *Sources whose strengths vary over their area.*

In all the preceding sections the strength of the source has been assumed to be constant over its area. If the strength of the source varies over its area the problem may be treated in the same way ; since there is no clear indication from physical considerations of the law of variation we confine ourselves to showing that for the simplest problem of this type, namely a band source of length $2l$ moving with velocity V in the x-direction in the plane $z=0$ of semi-infinite solid $z<0$ with no loss of heat from the plane $z=0$, the

* The comparisons with experiment are not very satisfactory since for fixed V and W it may be expected that μ and l will also depend on the sliding substances.

temperature distributions for various simple laws of variation which give the same total heat emission per unit time per unit length of the band are not very different.

If the strength of the source is $qf(x')$ we obtain as in §4 in place of (5) for the temperature in the plane $z=0$

$$v=\frac{q}{\pi K}\int_{-l}^{l} e^{-V(x-x')/2\varkappa}K_0\left\{\frac{V|x-x'|}{2\varkappa}\right\}f(x')dx'$$

$$=\frac{2\varkappa q}{\pi KV}\int_{X-L}^{X+L} e^{-u}K_0(|u|)f\left\{x-\frac{2\varkappa u}{V}\right\}du \quad \ldots\ldots\ldots\ldots \quad (55)$$

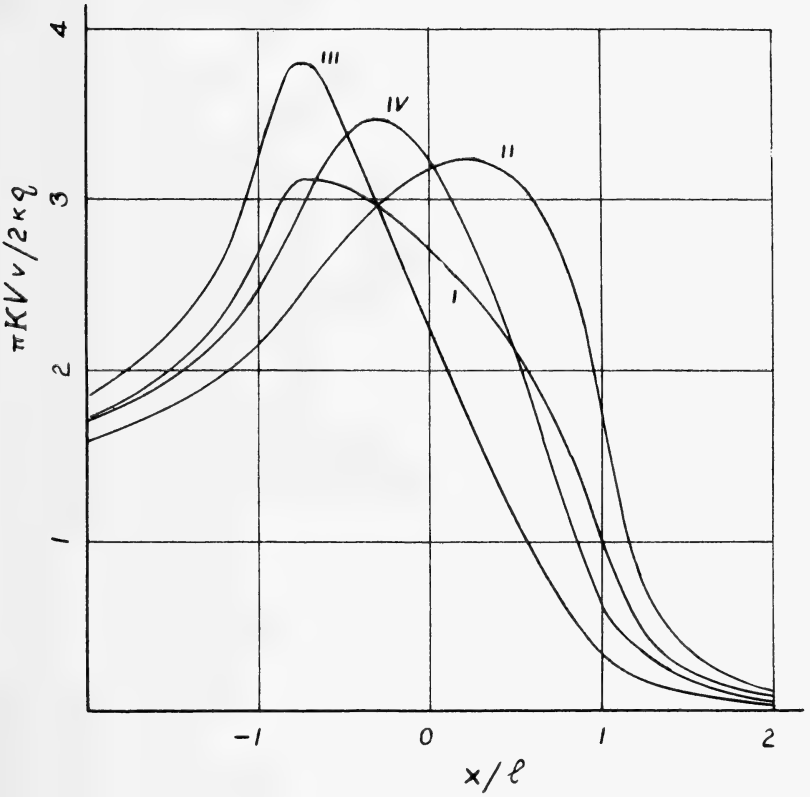

Fig. 9.

In Fig. 9, curves (i) . . . (iv) show $(\pi KVv/2\varkappa q)$ plotted against $\xi=x/l$ for the following cases :

(i) $f(x')=1$, the constant source previously discussed.

(ii) $f(x')=q(x'+l)/l$, a linear law with a maximum at the front of the band and zero at the rear.

(iii) $f(x')=q(l-x')/l$, a linear law with zero at the front of the band and a maximum at the rear.

(iv) $f(x')=3q(l^2-x^2)/(2l^2)$, a parabolic law.

The curves, though differing in shape, do not differ much in maximum or average temperatures, so it appears that the previous results for constant sources should give results of the right order of magnitude for any not too extreme law of variation.

13. *A case in which the velocity of the source is not constant.*

There is no difficulty in treating cases in which the position of the centre of the source is a given function $f(t)$ of the time; the strength of the source (taken to be uniform over its area) may either be constant, another arbitrary function of the time, or, as in the most important practical case, proportional to the velocity, say $Qf'(t)$ per unit time per unit area. Any case can be treated by the appropriate integration of (1) or (2).

As an example we determine the temperature at the centre of a band source which executes a simple type of relaxation oscillation. It has been suggested by Morgan, Muskat and Reed (*loc. cit.*), and others, that the stick-slip behaviour observed by Bowden and Leben may be due to relaxation oscillations in which the kinetic friction is less than the static friction. The simplest possible problem of this type, neglecting damping and assuming constant coefficients of friction, is the following: a mass m is held by force P against a plane which moves with velocity V, the coefficient of static friction is μ' and the coefficient of kinetic friction is μ, $\mu'>\mu$. Motion of the mass m parallel to the plane is resisted by a spring of stiffness mn^2.

We suppose the mass to be moving with the plane; this will continue until its displacement is

$$x_1=\frac{\mu' P}{mn^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (56)$$

when it will commence to slip backwards. Taking this time as the origin of time the new motion is given by

$$m(d^2x/dt^2)=-mn^2x+\mu P$$

with initial velocity V and initial displacement $\mu' P/mn^2$.

The displacement in this motion is

$$\frac{\mu P}{mn^2}+\frac{(\mu'-\mu)P}{mn^2}\cos nt+\frac{V}{n}\sin nt$$

and the velocity is

$$V\cos nt-\frac{(\mu'-\mu)P}{mn}\sin nt.$$

This motion continues until the relative velocity is zero, when sliding ceases; this happens at time

$$T_1=\frac{2\pi}{n}-\frac{2}{n}\tan^{-1}\frac{(\mu'-\mu)P}{mnV} \qquad \ldots\ldots\ldots\ldots \quad (57)$$

when the displacement is

$$x_2=\frac{(2\mu-\mu')P}{mn^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (58)$$

Relative rest continues for time

$$T_2=\frac{2(\mu'-\mu)P}{mn^2V} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (59)$$

and the process repeats.

As a numerical example, let $\mu'=0\cdot5$, $\mu=0\cdot45$, $P=400$ gm., $V=0\cdot006$ cm./sec., $m=0\cdot5$ gm., $n=2{,}000\pi$, so that $x_1=0\cdot0099$ cm., $x_2=0\cdot0079$ cm., $T_2=0\cdot33$ sec., $T_1=\pi/n=0\cdot0005$ sec., nearly.

Then in the slip region the displacement is approximately

$$0\cdot009+0\cdot001\cos 2{,}000\pi t,\ 0<t<0\cdot0005 \quad \ldots\ldots\ldots\ldots (60)$$

and this is followed by the long time T_2 of relative rest.

Thus to determine the temperature flash during slip we have to study the temperature due to a source whose centre executes the motion

$$\left.\begin{aligned} x&=a(1-\cos nt),\ 0<t<\pi/n \\ &=2a \qquad\qquad ,\ t>\pi/n \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots (61)$$

and in which the rate of heat generation is $Q(dx/dt)=Qan\sin nt$, per unit time per unit area.

For simplicity we determine the temperature at the centre of a band source of length $2l$, of this strength, and which has the motion (61) in the surface $z=0$ of a semi-infinite region with no loss of heat from the surface. If $t<\pi/n$, this is given by

$$\frac{Qan}{2\pi K}\int_0^t \frac{\sin nt'}{(t-t')}\,dt' \int_{-l}^{l} dx' \exp\left[-\frac{(a\cos nt'-a\cos nt-x')^2}{4\varkappa(t-t')}\right]$$

$$=\frac{Qan\varkappa^{\frac{1}{2}}}{2K\pi^{\frac{1}{2}}}\int_0^t \frac{\sin nt'dt'}{(t-t')^{\frac{1}{2}}}\left\{\operatorname{erf}\left(\frac{l+a\cos nt'-a\cos nt}{[4\varkappa(t-t')]^{\frac{1}{2}}}\right)\right.$$

$$\left.-\operatorname{erf}\left(\frac{-l+a\cos nt'-a\cos nt}{[4\varkappa(t-t')]^{\frac{1}{2}}}\right)\right\} \quad \ldots\ldots\ldots\ldots\ldots (62)$$

while if $t>\pi/n$ the temperature is

$$\frac{Qan\varkappa^{\frac{1}{2}}}{2K\pi^{\frac{1}{2}}}\int_0^{\pi/n} \frac{\sin nt'dt'}{(t-t')^{\frac{1}{2}}}\left\{\operatorname{erf}\frac{l+a+a\cos nt'}{[4\varkappa(t-t')]^{\frac{1}{2}}}\right.$$

$$\left.-\operatorname{erf}\frac{-l+a+a\cos nt'}{[4\varkappa(t-t')]^{\frac{1}{2}}}\right\} \quad \ldots\ldots (63)$$

In Fig. 10, curve I shows values of the temperature calculated from (62) and (63) for the case of a band source for which $l=0\cdot001$ moving in mild steel, $K=0\cdot144$, $\varkappa=0\cdot173$, its motion being given by (60), i.e. $a=0\cdot001$, $n=2{,}000\pi$, the rate of heat generation per unit time per unit area is taken to be that for a square slider with $l=0\cdot001$, $\mu=0\cdot45$, $P=400$ gm.

Curve II is the result which would be obtained by inserting the instantaneous velocity of the slider, namely, $2\pi\sin 2{,}000\pi t$, in the steady state formula (13) for the band source, with $X=0$; this naturally gives values which are too high, but since the discrepancy is not large it appears that by using the steady state formulæ in this way a fair approximation to the temperatures in non-steady motion may be obtained, provided the velocity is not too rapidly varying.

It should be added that curve I does not represent the actual temperature flash for a square mild steel slider with $l=0\cdot001$ moving as in (60) on a mild steel surface, since (i) the whole of the heat generated has been assumed above

to be taken by the surface (i.e. $\alpha=1$) while for the small values of L in question only about half will be, (ii) band source formulæ have been used in the region of small L where they give higher values than those for the square source, (iii) the temperature at the centre of the band and not the average temperature has been calculated. The temperature flash for a square source with $l=0\cdot001$ moving under the conditions above may be expected to be about 1/5 of that shown in Fig. 10, curve I.

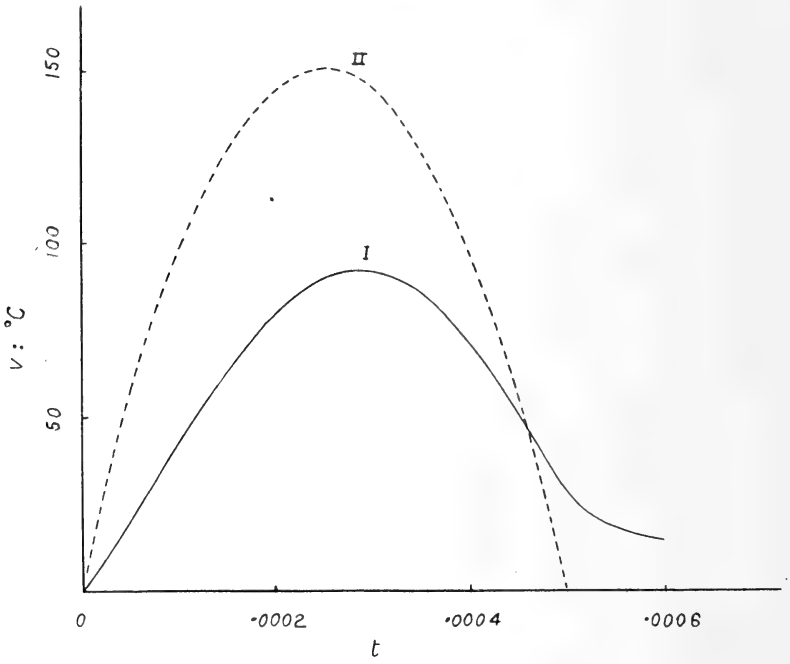

Fig. 10.

In conclusion I wish to thank Miss M. E. Clarke for her assistance with the computations.

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References.

Blok, 1937. *Inst. Mech. Eng.*, **2**, 222. (General discussion on Lubrication.)
Bowden and Ridler, 1936. *Proc. Roy. Soc.*, A, **151**, 610.
Morgan, Muskat and Reed, 1941. *J. Appl. Phys.*, **12**, 713.

A METHOD FOR THE ESTIMATION OF VEGETABLE MATERIAL IN SCOURED WOOL.

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With Plate VII.

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I. Introduction.

Greasy wool invariably contains vegetable material and the percentage of such vegetable "fault", as it is termed in the trade, varies considerably from district to district and from season to season. In appraising wool it is necessary to take into consideration the actual amount of "fault" present and for this reason a convenient method whereby it can be determined is of use. In the present paper a technique is described which fulfils this purpose and enables rapid and reasonably accurate routine estimations to be carried out on scoured wool samples.

In commercial carbonising, the plant material is degraded to carbon by baking the "faulty" wool in the presence of acid (usually sulphuric acid) and the carbon together with some wool is removed in specially designed machines. The application of this procedure to the laboratory presents difficulties in the removal of the carbonised vegetable material without loss of wool, the use of special machinery, or tedious hand picking. The loss in weight in wool would also affect the results and this loss varies when different types of wool are treated. The method therefore is unsuitable and inconvenient for the accurate routine estimation of vegetable matter in wool.

Methods which depend upon the removal of the wool by caustic soda solution have not been found satisfactory as the vegetable material suffers substantial losses in weight and on recovery is almost unrecognisable and usually covered with a gelatinous layer of undissolved protein.

A useful procedure for ascertaining the *nature* of the vegetable matter present in a sample of scoured wool is to immerse the sample in a liquid of the same refractive index as wool (e.g. orthodichlorbenzene). This renders the wool invisible and the contained vegetable matter is clearly brought to view. The establishment of a test of this type on a quantitative basis involving light measurements presents difficulties due to large variations in the physical, especially the visual, properties of the vegetable material present in the wool. This is clearly illustrated in Plate VII, which shows the difference in appearance between the same weights of some of the various burry materials found in wool. It can be seen from this that the solid Bathurst burr, if present in the wool and examined by a method of light measurement, would appear less than the same weight of the lighter Trefoil burr or Khaki weed. An examination of this plate also clearly indicates the difficulties associated with visual and manual estimation of the percentage of vegetable matter in wool.

In developing the method described below, a study was made of the serious damage which occurs to wool when it is treated with hydrogen peroxide in the presence of certain metallic salts (a fact well known to most wool bleachers). Investigations along these lines revealed that the wool after degradation by such oxidising agents under certain conditions was readily soluble in dilute solutions

of sodium carbonate and certain other alkalis. From the solution so obtained the contaminating vegetable material could be readily separated by simple filtration.

II. Description of the Method.

All chemicals used were C.P. quality with the exception of the hydrogen peroxide, which was prepared by dilution of the commercial (100 vol.) product.

A 20–30 gm. sample of scoured wool containing vegetable matter is immersed in a solution consisting of 500 ccs. of 6 per cent. hydrogen peroxide, 25 ccs. of 5 per cent. copper sulphate and 8 ccs. of 5 per cent. sodium bicarbonate. The wool is thoroughly wetted at room temperature with the solution, which is then raised to the boil by heating for 5 minutes with stirring. Boiling is continued for 2 minutes with stirring and the wool, which is considerably degraded and now appears brownish in colour, is removed from the solution, squeezed and washed with water. It is then opened out by hand and placed in 600 ccs. of 1 per cent. solution of sodium carbonate (anhydrous) maintained at 95–100° C. and stirred for 2 minutes. This procedure completely dissolves the wool and the intact vegetable matter is left behind. The latter is removed by means of a 40 mesh sieve* washed thoroughly under running water, dried and weighed.

III. Discussion.

The initial degradation of the wool by means of hydrogen peroxide, as specified above, has been found to depend considerably upon the pH value of the solution. Figures illustrating this fact are recorded in Table 1, which shows the losses in weight occurring at different pH values as determined by the glass electrode method. The experiments were carried out as described above with variations in the amount of sodium bicarbonate solution used. The oven dry weight of wool was determined before and after each treatment and the percentage loss in weight was then calculated.

Table 1.

Effect of pH on the Peroxide Treatment of Wool.

Amount of 5 per cent. $NaHCO_3$ Solution. (cc.s.)	pH Value.	Loss in Weight. (Per Cent.)
0	2·5	21·2
5	3·9	26·0
8	4·2	41·0
12	4·6	37·3
15	4·9	30·9
25	5·8	23·2

The figures in Table 1 show that for best results the pH value of the solution should be within the range 4·0–4·6. The optimum effect is at pH 4·2, where the wool is considerably degraded and if dried can be powdered with ease.

Owing to variations in the pH value of commercial hydrogen peroxide it may be necessary to add a slightly different amount of sodium bicarbonate from

* This size has satisfactorily collected the usual type of burry material. An 80 mesh sieve is required for very fine grass seed.

that specified in order to obtain the optimum pH value. A useful indication of the latter is when a brown precipitate (probably copper oxide) just forms and does not re-dissolve on shaking the solution.

It has been found that there is no noticeable change in appearance of vegetable matter when recovered by the above method. There is, however, a loss in weight during recovery for which due allowance must be made in calculating the final results. Table 2 contains the percentage recoveries obtained when the method was applied to known weights of the common types of vegetable material introduced into wool which was burr free. (The latter was obtained from a dry combed 60's top.)

TABLE 2.

Recoveries of Vegetable Material.

Type of Vegetable Material.	Recovery (Per cent.).
Noogoora burr (*Xanthium chinense*) ..	96
Ring burr (Queensland) (*Sida platycalyx*)	96
Bathurst burr (*Xanthium spinosum*) ..	94–95
Basket or barrel clover (*Medicago truncatula*)	92
Straw (*Triticum vulgare*)	81–90
Trefoil clover (*Medicago hispida denticulata*)	80–89
Cut leaf clover (*Medicago laciniata*) ..	83
Small trefoil clover (*Medicago minima*) ..	78–83
Barley grass (*Hordeum murinum*) ..	71–80
Twigs (probably of *Eucalyptus* spp.) ..	78–85
Saffron thistle (*Carthamus lanatus*) ..	78
Shive (*Aristida* spp.)	68–74
Subterranean clover (*Trifolium subterraneum*)	69–73
Khaki weed (*Alternanthera echinata*) ..	71
Corkscrew grass (*Erodium cygnorum*) ..	69–71

It can be seen that these recovery figures fall within a narrow range for each type, and they can therefore be used to deduce certain factors which are applied in the working out of results. For convenience the vegetable material has been divided into three major groups which are most common in Australian fleeces, and the results are corrected according to the nature of the recovered vegetable matter. The first group contains the hard Noogoora and Bathurst burrs, factor 1·05. The next group contains the Trefoil clover burrs, factor 1·18. The third group contains the fine grass seeds and shive, factor 1·43. In each instance the dry weight of recovered vegetable material is multiplied by the appropriate factor and the final result is usually expressed to the nearest 0·5 per cent. Generally it is found that one of the above three groups will predominate in the vegetable material recovered from each scoured fleece sample. Occasionally there are mixtures and the factor may be altered accordingly, but slight variations in its value will not seriously affect the final result as the burr is usually present as a minor percentage in the wool-burr mixture.

IV. CONCLUSION.

A method has been developed and adopted as a laboratory routine for estimating the percentage of vegetable material in wool. The method possesses the advantages of speed and ease of manipulation without the use of any special mechanical apparatus. The usual time required to remove completely the

vegetable material from the wool is about 12 minutes, and one laboratory worker can conveniently carry out about 20 complete analyses per day.

Preliminary experiments have shown that the method should also be applicable to the determination of cotton in cotton and wool mixtures and its use for removing wool from mixtures with other fibres is also being investigated.

V. Acknowledgments.

Thanks are due to the Central Wool Committee for permission to publish this paper. I also wish to record appreciation of the helpful interest and encouragement of Mr. J. R. McGregor during the course of the work.

The constructive criticism and suggestions of Mr. M. R. Freney, Officer-in-Charge, Central Wool Committee Testing House, are gratefully acknowledged.

I am indebted to Mrs. E. S. Emerton for her willing assistance with the experimental work.

Explanation of Plate VII.

Showing the relative appearances of 20 gm. of—

1. Bathurst burr (*Xanthium spinosum*).
2. Trefoil clover (*Medicago hispida denticulata*).
3. Small Trefoil clover (*Medicago minima*).
4. Khaki weed (*Alternanthera echinata*).

1
2
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CONTENTS

VOLUME LXXVI

Part IV

Page.

ART. XIX.—A Revision of Certain Species of Leptospermeæ. By Edwin Cheel. (Issued August 2, 1943) 229

ART. XX.—Physiography of the Wellington District, N.S.W. By Margaret J. Colditz, B.Sc. (Issued August 2, 1943) 235

ART. XXI.—Upper Ordovician Graptolite Horizons in the Yass-Jerrawa District, N.S.W. By Kathleen Sherrard, M.Sc. (Issued August 2, 1943) 252

ART. XXII.—Permian Bryozoa of Eastern Australia. Part III. Batostomellidæ and Fenestrellinidæ from Queensland, New South Wales, and Tasmania. By Joan M. Crockford, M.Sc. (Issued August 2, 1943) 258

ART. XXIII.—The Action of Solvents on Torbanite and the Nature of Extracted Products. By J. A. Dulhunty, B.Sc. (Issued August 2, 1943) 268

ART. XXIV.—The Chemistry of Bivalent and Trivalent Rhodium. Part VI. Pyridine Complexes of Rhodous Halides. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued August 2, 1943) 275

ART. XXV.—A Note on the Magnetic Behaviour of Potassium Cyanonickelite. By D. P. Mellor, M.Sc., and D. P. Craig, M.Sc. (Issued June 28, 1943) 281

ART. XXVI.—Functional Relations between Scrotum and Pouch and the Experimental Production of a Pouch-like Structure in the Male of *Trichosurus vulpecula*. By Adolph Bolliger, Ph.D. (Issued August 2, 1943) 283

ART. XXVII.—Co-ordination Compounds Derived from Nicotinylacetone. By Francis Lions, B.Sc., Ph.D., Benjamin S. Morris, M.Sc., and Ernest Ritchie, M.Sc. (Issued September 1, 1943) 294

ART. XXVIII.—Progressive Rates of Tax in Australia. II. By H. S. Carslaw. (Issued September 1, 1943) 304

ART. XXIX.—Galileo and Newton : Their Times and Ours. By Professor O. U. Vonwiller. (Issued September 1, 1943) 316

ART. XXX.—Chemistry of the Earth. By J. S. Anderson, Ph.D. (First Liversidge Lecture.) (Issued September 1, 1943) 329

ART. XXXI.—The Imperfect Crystal. By J. S. Anderson, Ph.D. (Second Liversidge Lecture.) (Issued September 1, 1943) 345

TITLE PAGE, CONTENTS, NOTICES, PUBLICATIONS i

OFFICERS FOR 1942-43 vii

LIST OF MEMBERS, AWARDS OF MEDALS, ETC. ix

ABSTRACT OF PROCEEDINGS xxi

PROCEEDINGS OF THE SECTION OF GEOLOGY xxxiv

INDEX TO VOLUME LXXVI xxxv

A REVISION OF CERTAIN SPECIES OF LEPTOSPERMEÆ.

By Edwin Cheel.

With Plates VIII-XII.

Manuscript received, October 16, 1942. Read, November 4, 1942.

From a critical survey of the tribe Leptospermeæ of the family Myrtaceæ in Bentham's *Flora Australiensis*, it will be seen that there are two special characteristics which distinguish the genera. In the five genera—*Scholtzia*, *Bœckea*, *Astartea*, *Hypocalymna* and *Balaustion*—the leaves are opposite. The genera *Agonis*, *Leptospermum* and *Kunzea* are distinguished from the five genera mentioned above by having alternate leaves. It is in regard to the last three genera with free stamens that I propose to offer some remarks.

In Bentham's key to the genera, the main distinctions are as follows :

Flowers sessile in globular heads. Stamens free, definite, or if indefinite none opposite the centre of the petals : *Agonis*.
Flowers solitary or crowded, but not in heads : *Leptospermum*.
Flowers closely sessile. Stamens exceeding the petals : *Kunzea*.
Exceptions are made in some species of *Kunzea* for the flowers being " closely sessile ".

Field observations and the examination of a large series of herbarium specimens have shown that there are at least six species classed in the genera *Bœckea*, *Agonis*, *Kunzea* and *Leptospermopsis*, which would cause less confusion if they were transferred to the genus *Leptospermum*. In a previous paper (Cheel, 1931) reference was made to the genera *Fabricia* and *Pericalymma*, formerly classed as distinct genera which were retained by Bentham (1866) as sections of the genus *Leptospermum*. Bentham also remarked that although there is a marked difference in the shape of the seeds, he had concluded this to be rather a sectional than a generic character. The genus *Agonis*, as stated by Baillou (1880), " was formerly confounded with *Leptospermum* ; it is distinguished by the stamens, often less numerous, and the ascending ovules, two to four in number, inserted on a placenta itself ascending ; differential characters which, in this group, are of little value, and which, doubtless, we should consider too insignificant to establish a distinct genus, if the flowers were not grouped in small globular capitules, axillary and terminal ". It is also stated by Bentham (1866) " that the genus *Agonis* is limited to West Australia, and that it was formerly considered as a section of *Leptospermum*, on account of its alternate leaves and stamens not exceeding the petals ". In the section Ataxandrea of *Agonis* the flowers have 20 to 30 stamens, but none opposite the centre of the petals, hence the species. *Leptospermum brachyandrum* (A. Cunn.) Cheel (see Pl. XII, B, fig. (*d*)) simulates some of the characteristics of *Bœckea* but has not the opposite leaves.

The descriptions of several species of *Leptospermum* as drawn up by Bentham (1866) are of a composite nature, so as to include those species which he (Bentham) remarked " are very difficult to distinguish, and that different as some of them appear to be at first sight, pass so gradually one into the other that they might be readily admitted as varieties of one species, whilst on the other hand, many of the varieties which are enumerated in the Flora Australiensis had been distinguished as species by Robert Brown ".

Our knowledge requires yet to be perfected in reference to the permanency of some of the characteristics assigned to species of such genera as *Agonis*, *Kunzea* and *Leptospermum*, because here in a comparatively young country the whole cyclus of forms within which species range, particularly in distinctive regions so extensively varied as ours are, are not in all cases sufficiently ascertained. The study of the living plant is less bewildering than the study of herbarium specimens described in literature, because we have first-hand evidence of the effects of light and shade or other environmental conditions in the field which we do not get from herbarium specimens. Many species were described by European specialists who had not had the opportunity of examining the plants in their natural surroundings, consequently they were entirely dependent on dried herbarium material which in many instances was too fragmentary, and so, many of the species were founded on meagre information.

The two species of *Kunzea*, viz. *K. corifolia* and *K. peduncularis*, which are illustrated (Pl. X, figs. A and B) show that the flowers are not sessile in globular heads. The latter species was classified by A. Cunningham in the genus *Bœckea*, but as the leaves are not opposite, and the flowers not sessile in globular heads, the species is better classed in *Leptospermum* than in *Bœckea* or *Kunzea*, as *Leptospermum phylicoideum*, Cunningham's specific name having twelve years' prior claim over that of Mueller.

In 1793 the noted English botanist, James Edward Smith (afterwards Sir James Edward) described *Leptospermum ambiguum*. This species was transferred to the genus *Kunzea* as *K. corifolia* by Reichenbach (1828) and was adopted by Bentham. Although the stamens exceed the petals in both the above species, the character is too insignificant to be considered of real generic value, especially as the flowers are not sessile in globular heads.

In a previous paper (Cheel, 1931, p. 200) attention was drawn to *Leptospermopsis*, a genus founded by Spencer le Moore (1920). The type of the genus was based on specimens collected by Maxwell in Western Australia, having five stamens, one opposite the centre of each petal. It is noteworthy that Mueller (1856) described Maxwell's specimens under the name *Kunzea podantha*, stating that the number of stamens varied from 5 to 15, and that the species was allied to *Kunzea peduncularis*, *Kunzea brachyandra* and *Leptospermum brevipes*. There has been considerable confusion concerning these three species. The last was regarded by Bentham (1866) as a synonym of *Leptospermum attenuatum* and by Miquel (1856) as a synonym of *Leptospermum flavescens*. The species *Kunzea podantha* F. v. M., was reduced by Bentham *l.c.*, to a variety of *L. erubescens* as *Leptospermum erubescens* var. *psilocalyx*. Diels (1920) rehabilitated the plant to specific rank, as *Leptospermum podanthum*. Mueller, in describing *Kunzea peduncularis*, evidently overlooked the fact that the species had already been described by A. Cunningham (1843) under the name *Bœckea phylicoides*. The latter name was included by Bentham (1866) as a synonym of *Kunzea peduncularis*.

In his description of *Leptospermum abnorme* F. v. M., Bentham (1866) states " stamens about 25, crowded opposite the sepals, solitary opposite the petals ". It is interesting to note than Bentham also draws attention to the species of *Agonis* in Section I, Taxandria, " having stamens 10, regularly opposite the calyx-lobes, and petals as in the first two sections of *Bœckea*". The species was originally described by Mueller (1860) as *Kunzea brachyandra*, but was afterwards changed to *Leptospermum abnorme* ; the latter name was adopted by Bentham, but as the specific name " *brachyandra* " has six years' priority, it should, according to botanical rules, be adopted as *Leptospermum brachyandrum* (see Cheel, 1931).

Leptospermum brevipes F. v. M.

The original description of Mueller (1854-55) is as follows: Branches glabrous, or in a young state somewhat silky; leaves flat, oblong-lanceolate, very short pointed, glabrous, three-nerved, full of oil dots; flowers solitary or twin, axillary or on very short branchlets, terminal; pedicels and calyces grey silky-pubescent, the former as long or longer than the latter; lobes of the calyx pubescent, lanceolate; capsule depressed, five-celled. Generally a companion of *Kunzea peduncularis*, to which it bears more resemblance in habit than to any of its congeners, being quite anomalous in producing very conspicuous flower stalks. It ranks nearest to *L. divaricatum*.

It is recorded from Ovens River by Mueller but is listed as a synonym of *L. flavescens* by Miquel (1856) and as a synonym of *L. attenuatum* by Bentham (1866). The localities " Avon, Mitta-Mitta, Ovens, and other rivers in Gippsland, Victoria ", quoted by Bentham under *L. attenuatum* are those of type specimens of *L. brevipes*. Specimens from Medlow, N. S. Wales, collected by J. H. Maiden (see Pl. IX, B, (*a*)-(*e*)) belong to this species. A note by the late Mr. E. Betche is as follows: " These are all specimens of the small fruited Leptospermum with long leaves and glabrous calyx. According to Bentham's Flora, it can only be *L. flavescens*, or must be a new species. In shape of fruits and leaves it resembles very much *L. attenuatum* Sm., but *L. attenuatum* belongs to the group with hairy calyx and has longer pedicels."

In Miquel (1856) *L. brevipes* is listed as a synonym under *L. flavescens*, with the locality stated as " Buffalo Creek, Owen's River ". It would appear from the above and the statement " Mount Aberdeen, Tasmania ", as the location for *K. leptospermoides*, that there has evidently been some mix up, especially as in the description of *K. peduncularis*, published in Miquel, the capsules are stated to be " five loculares ". The capsules of *L. brevipes* are normally five-celled, as illustrated in Pl. IX, B, (*a*)-(*e*).

Additional specimens of this species represented in the National Herbarium, Sydney, are from the following localities:

New South Wales: Mount Wilson, Medlow, Wentworth Falls, Leura, Mount Victoria, Mount Tomah, Cassilis (15 miles south), Delegate, Wombeyan Caves.
Victoria: Buffalo Mountain.
Federal Territory: Near the Cotter River.

Leptospermum phylicoideum (A. Cunn.) Cheel (*Kunzea peduncularis* F. v. M.).

In 1843, Allan Cunningham in Schau (1843) described some plants found on the banks of rivers in Argyle County, under the name *Bœckea phylicoides*. The species was apparently unknown to Mueller, who in 1855 described the same species under the name *Kunzea peduncularis* as follows: " Erect, glabrous or rarely downy; leaves crowded, coriaceous, perforated by oil-glands, linear or oblong-lanceolate, acute, one-nerved; flowers white, axillary, solitary, stalked, crowded below the summit of the branches or forming terminal corymbs; bracts downy lanceolate-linear, deciduous; petals twice as long as the deltoid segments of the calyx, and half as long as the stamens; capsule with three, four or five cells, immersed in the dry campanulate calyx; ripe seeds hardly shining, reticulate."

Mueller's plants were collected " at the foot of the Australian alps, on the banks of rivers and rivulets. Leaves and flowers are similar to those of *Kunzea corifolia*; fruit is smaller and nearly campanulate; its stalk is sometimes thrice the length of the calyx ". Bentham (1866) adopted Mueller's name, *K. peduncularis*, listing *Bœckea phylicoides* as a synonym. In a description published in Miquel (1856) the capsules of *K. peduncularis* are described as

" five loculari ", and that it differs from the preceding species (*K. leptospermoides*) in having larger leaves and longer pedicels (*foliis majoribus pedicellis longioribus*). The locality is stated as " Mount Aberdeen, Tasmania ". *Kunzea leptospermoides* F. v. M. in Miquel is listed as a synonym of *K. peduncularis* by Bentham, and a variety *K. peduncularis* var. *brachyandra* is described from " summits of the White Rock Mountains, Mount Aberdeen, and sources of the Genoa River ", with the following description : " stamens shorter, but still exceeding the petals. Leaves oblong linear ". Specimens labelled *K. leptospermoides* in the National Herbarium, Sydney, collected by Mueller in Victoria (*Austral felix*) and Templestone, Victoria, have narrower leaves than *K. peduncularis*, and are probably the var. *brachyandra* of Bentham. In Miquel (1856) the species is kept as a distinct species, and is listed from " Mount Aberdeen, Tasmania ", which appears to be an erroneous location.

Specimens which may be regarded as typical of *Bœckea phylicoides* A. Cunn., which was afterwards described as *Kunzea peduncularis* by Mueller and adopted by Bentham, are represented in the National Herbarium, Sydney, from the following localities :—New South Wales : Bathurst, R. H. Cambage (No. 1211) (see Pl. X, B) ; Burrenjuck (see Pl. X, B), which show pedicellate flowers and normally three-celled capsules. The species is illustrated by Nidenzu in Engler and Prantl (1898) and it is shown to have some stamens as long as the petals and some longer than the petals, and the capsules three-celled. In the key to the genera, Bentham (1866) states : " Flowers closely sessile (except in some species of Kunzea). Flowers in heads or solitary, or rarely in short spikes," and places *Kunzea peduncularis* and *K. corifolia* in section II, Salisia, as follows : Flowers pedicellate . . . *K. peduncularis* ; flowers sessile . . . *K. corifolia*. It will be seen from the above that there is considerable confusion in placing these two species in the genus *Kunzea*, especially when it is seen from the drawing I have made showing Pl. X, A and B, that although exception is made for some species by Bentham, the flowers are not sessile as stated in Bentham's key for *K. corifolia*. Although the stamens exceed the petals in both species, the flowers are distinctly pedicellate and not " closely sessile in compact heads " as in other species of the genus.

In view of the discrepancies in the descriptions of the three species as published in Miquel (1856) *K. peduncularis*, *K. leptospermoides* and *Leptospermum brevipes*, and the classification of the latter species as a synonym under two different genera, I propose to adopt the original classification of the noted English botanist, Sir James Edward Smith, viz. " *Leptospermum ambiguum* " (1793) and Allen Cunningham's specific name " *phylicoides* " as having prior claim over " *peduncularis* ". I propose that the species should be classed as *Leptospermum phylicoideum*.

Leptospermum brevipes F. v. M. is a distinct species, having capsules with normally five cells.

Leptospermum multicaule A. Cunn. (1825) (*L. myrtifolium* Sieb.) in D.C. 1828.
L. myrtifolium (Sieb.) Cambage (1919), 707.

Cunningham's (1825) specific name " *multicaule* " has priority over Sieber (1828). The records of Bentham (1866) giving the localities Bathurst and Blue Mountains, New South Wales, are probably correct, but it is very doubtful if the Tasmanian and Queensland localities mentioned are correct, as we have no specimens from either of these two States represented in herbaria. There are specimens from Wombeyan Caves collected by R. H. Cambage and E. Cheel, and from Corang River, near Braidwood, E. Cheel ; also from Mullion Creek, near Orange, R. H. Cambage (No. 666). The species also extends to the Federal Territory (near Tamgar) collected by Miss Arnott, and to Snowy River, collected by Miss Hudson.

References.

Baillon, H., 1888. "The Natural History of Plants."
Bentham, G., 1866. *Flora Australiensis*, 3.
Cheel, E., 1919. *J. Roy. Soc. N.S.W.*, **53**, 122.
Cheel, E., 1931. *J. Roy. Soc. N.S.W.*, **65**, 201, 203.
Cunningham, A., 1825. In Field's New South Wales.
Cunningham, A., 1843. In Schau. Walper's *Repertorium Botanices*, **2**, 291.
Diels, L., 1920. In Engler's *Botanische Jahrbucher*, **35**, 423.
Druce, G. Claridge, 1917. Report of Botanical Exchange Club, British Isles.
Miquel, F. A. W., 1856. *Ned. Kruidk. Arch.*, **4**, 146.
Mueller, F. v. M., 1855. *Trans. Vict. Inst.*, **1**, 125.
Mueller, F. v. M., 1856. In Miquel, *Ned. Kruidk. Arch.*, **4**, 146.
Mueller, F. v. M., 1860. *Fragmenta Phytographia*, **2**, 28.
Moore, Spencer L., 1920. *J. Linn. Soc.*, Botany, London, **45**, 12.
Nidenzu, Franz, 1898. In Engler and Prantl, *Pflanzenfam*, 3, Teil Abt. 7, 95, Fig. 41, A-F.
Reichenbach, H. G., 1828. *Conspect.*, 175.
Sieber, F. W., 1828. In *D.C. Podr.*, **3**, 238.
Smith, J. E., 1793. *Exot. Bot.*, Tab. 59.
Smith, J. E., 1797. *Trans. Linn. Soc.*, **3**, 264.
White, C. T., and Francis, W. D., 1920. *Dept. Agric. Queensland, Bot. Bull.* 22, 16.

Explanation of Plates.

Plate VIII.

Leptospermum multicaule A. Cunn.

A. (*Leptospermum myrtifolium* Sieb.)

(*a*) Twig showing clustered leaves.
(*b*) Flower unexpanded.
(*c*) Capsule showing five valves slightly raised above the rim of calyx-tube.
(*d*) Flower fully expanded showing five petals and numerous stamens.
(*e*) Flower with petals removed to show calyx-lobes.

B. *Leptospermum trivalvum* Cheel (1931), 201.

(*a*) Twig showing clustered leaves with flowers *in situ*.
(*b*) Capsule showing three valves opened to shed the seeds and persistent calyx-lobes.
(*c*) Flower unexpanded.

C. *Leptospermum*.

(1) Fertile and abortive seeds of *L. odoratum* Cheel (1919), 122.
(2) Fertile and abortive seeds of *L. Roei* Benth.
(3) Fertile and abortive seeds of *L. phylicoideum* (A. Cunn.) Cheel.
(4) Fertile (winged) and abortive seeds of *L. lævigatum* F. v. M.

Plate IX.

A. *Leptospermum Mjobergii* Cheel (1919), 120.

(*a*) Flowering twig. (Nat. size.)
(*b*) Leaf enlarged to show five longitudinal veins and oil-glands.
(*c*) Flower bud unexpanded.
(*d*) Flower showing back view of calyx-lobes comparatively smooth and calyx-tube distinctly pilose. Underside of petals slightly exceeding the calyx-lobes.
(*e*) Flower with four petals removed and four calyx-lobes removed to show three stamens opposite petal and one stamen opposite calyx-lobe. Style in centre of six-valved ovary.
(*f*) Capsules in axils of leaves.
(*g*) Capsule with style not fully matured showing raised valves pilose on surface.

B. *Leptospermum brevipes* F. v. M. (1855).

(*a*) Flowering twig natural size with abbreviated pedicellate flower and capsule.
(*b*) Flower enlarged to show comparatively smooth calyx-tube and short pedicel and calyx-lobes in comparison with the petals and stamens.
(*c*) Vertical section of flower.
(*d*) Calyx-tube and style with capitate stigma.
(*e*) Capsule with five valves slightly opened.

PLATE X.

Leptospermum ambiguum Sm. (1793).
(*Kunzea corifolia* Reichb.)

(A. *Kunzea ambigua* (Sm.) Druce.)

(*a*) Portion of a twig with leaves and terminal cluster of flowers, stamens much exceeding the petals.
(*b*) Mature capsules with persistent calyx-lobes.

B. *Leptospermum phylicoideum* Cheel (n. comb.).
(*Bœckea phylicoidea* A. Cunn., 1843.)

(*a*) Flower slightly enlarged with elongated pedicel singly in axil of the leaf.
(*b*) Capsules fully matured (slightly enlarged). Note the hispid leaves, pedicels and calyx-tube.

PLATE XI.

A. *Leptospermum Whitei* Cheel (1931), 199.
(*Agonis elliptica* White and Francis.)

(*a*) Flowering twig with two mature capsules and (*b*) persistent scaly bracts (?), bristly hairs at base of leaves.
(*b*) Leaves enlarged to show venation and bracts.
(*c*) Flower dissected from the cluster (*a*) showing pilose calyx-tube and calyx-lobes, also stamens.

B. *Leptospermum semibaccatum* Cheel (1931), 203.

(*a*) Twigs with leaves only.
(*b*) Twig with slightly enlarged leaves and capsule.
(*c*) Twig with three mature capsules five-valved.

PLATE XII.

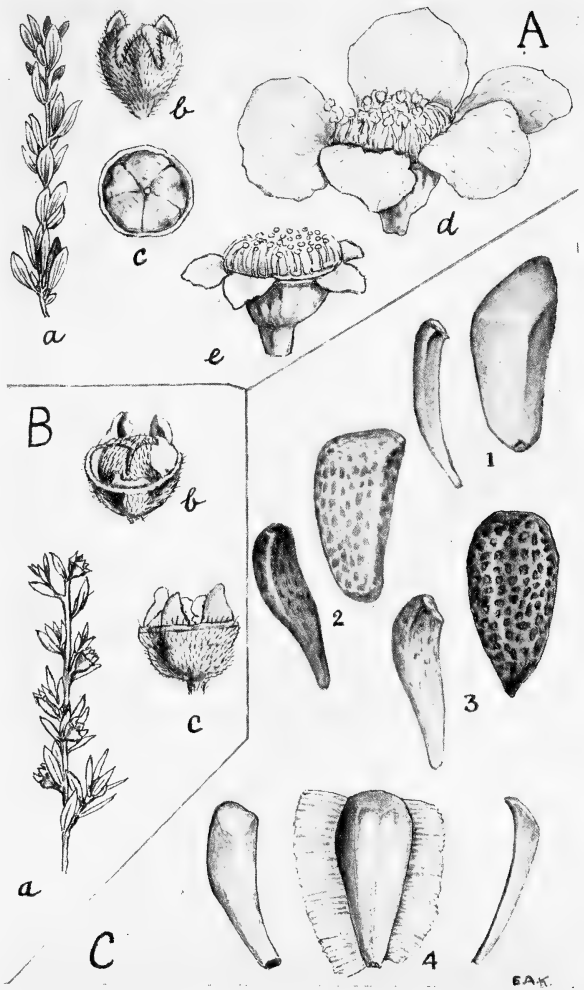
A. *Leptospermum.**
(*Agonis Scortechiniana* F. v. M.)

(*a*) Flowering twig (nat. size) with terminal fasicles of flowers.
(*b*) Flower showing hispid calyx-tube, five petals and stamens.
(*c*) Two floral bracts hispid on outer surface, smooth inner side.
(*d*) Capsules three-celled.

B. *Leptospermum brachyandrum* Cheel (1931), 197.

(*Kunzea brachyandra* F. v. M. *Agonis abnormis* C.T.W. and W.D.F., 1920.)
(*a*) Twig with terminal fasicle of flower and a flower singly in axil of leaf.
(*b*) Calyx-tube and persistent calyx-lobe with bristly hairs.
(*c*) Style with enlarged almost three-lobed stigma.
(*d*) Flower (enlarged) with three-five stamens opposite sepals and one opposite the petals.
(*e*) Byron Bay W.F. A form with narrow-pointed leaves.
(*f*) Twig with fully matured three-valved capsules.

* Since the submission for publication of this paper, Mr. C. T. White, Government Botanist of Queensland, who has seen the original specimen collected by A. Cunningham at Moreton Bay, Qld., in 1824, described as *Leptospermum speciosum* Schauer (*Melaleuca leucadendron* L. var. *parvifolia* Benth. in part), states that there is no question about its identity with *Agonis scortechiniana* F. v. M. See *Proc. Roy. Soc. Qld.*, 1942, p. 218.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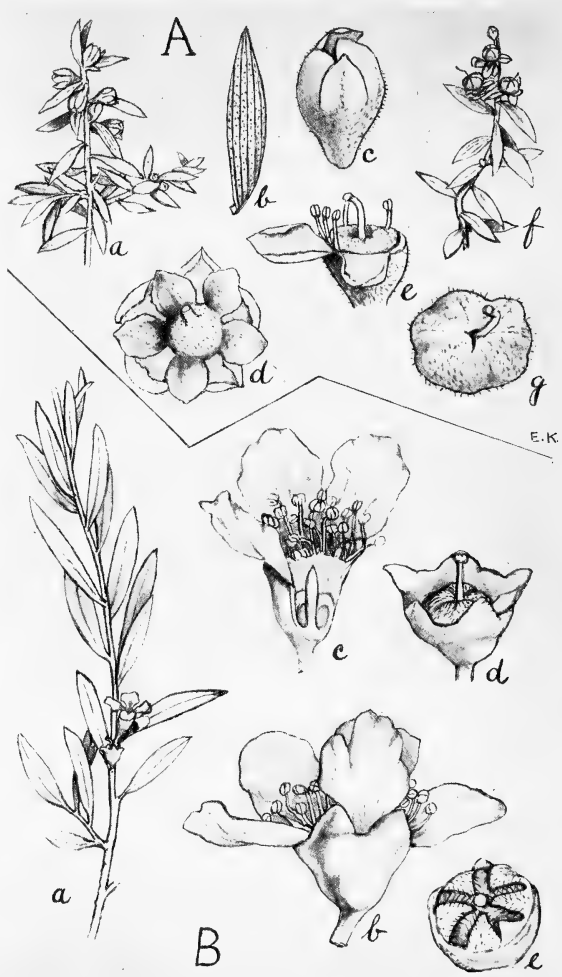
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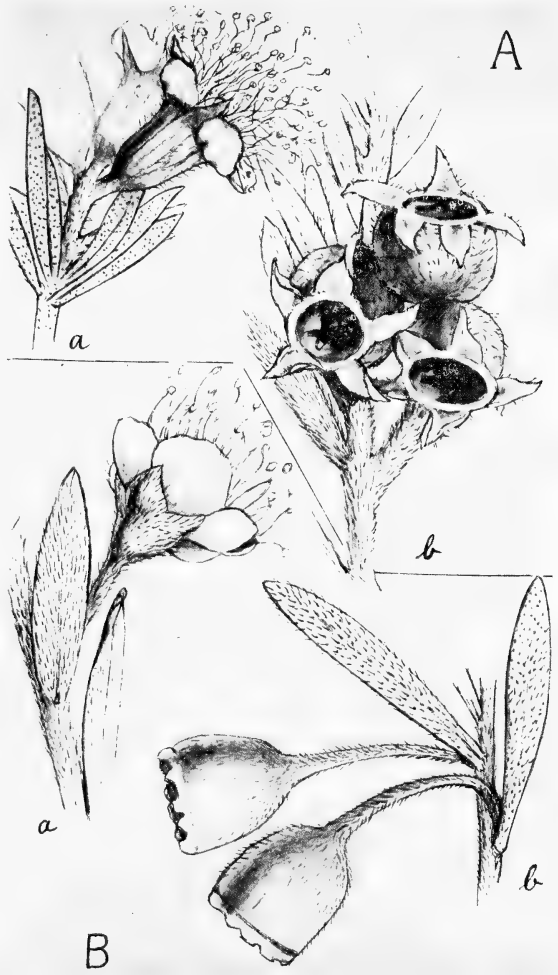
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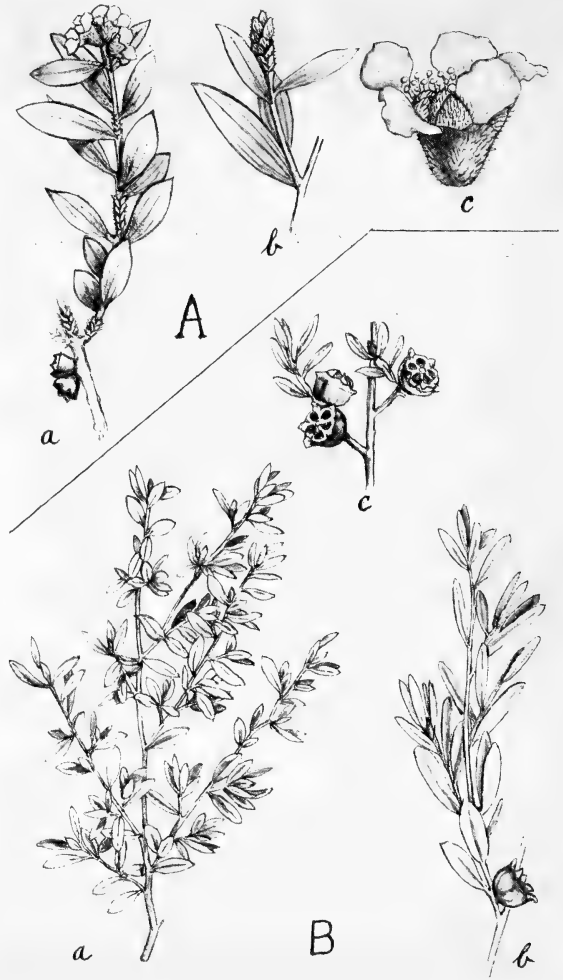
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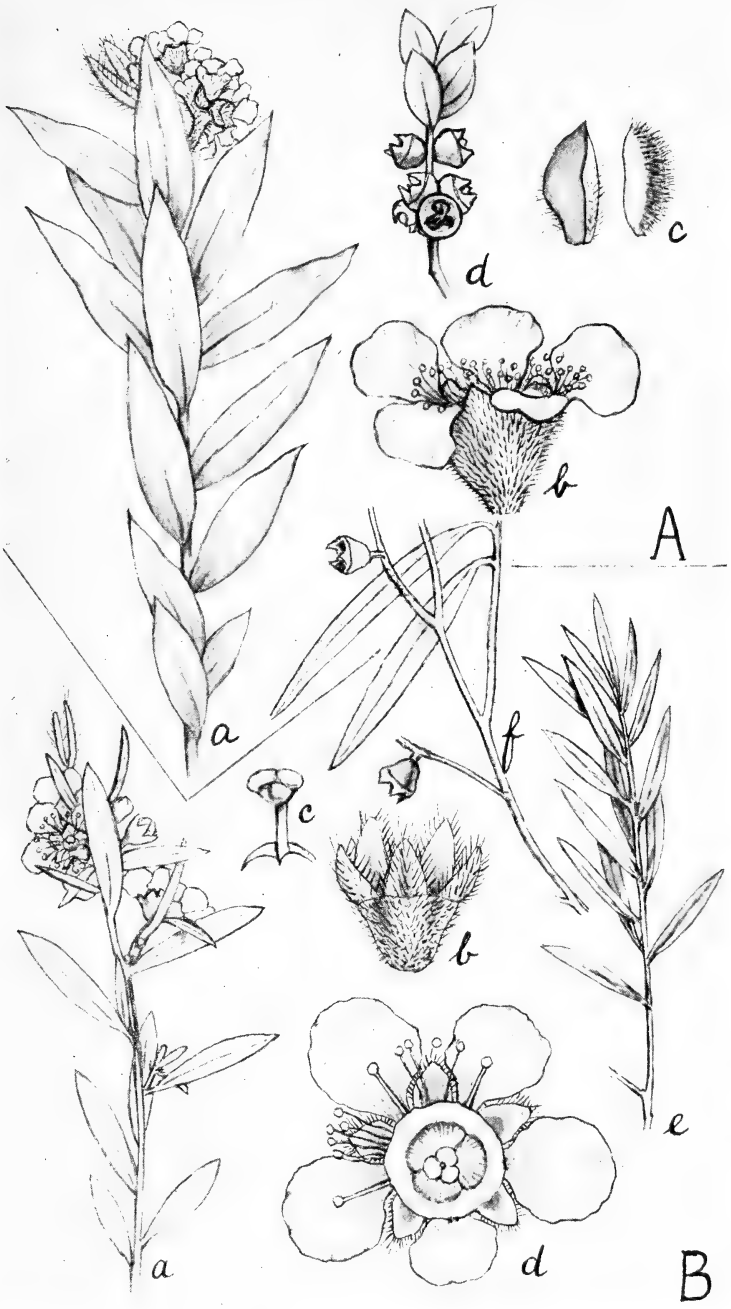
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PHYSIOGRAPHY OF THE WELLINGTON DISTRICT, N.S.W.

By Margaret J. Colditz, B.Sc.

With Plates XIII-XIV.

Manuscript received, November 11, 1942. Read, December 2, 1942.

Contents.

	Page
1. Introduction	235
2. General Geology and Structure	238
3. Tertiary Basalt	238
4. Alluvial Deposits	239
5. Topography	240
6. Drainage System—	
(i) General	242
(ii) Valley Form in Relation to Geological Structure	243
(*a*) The Macquarie River	243
(*b*) The Tributaries of the Macquarie River	244
7. Erosion Surfaces	245
8. Age of Erosion Surfaces	248
9. Interpretation and History	249
10. Summary	250
11. References	250

1. Introduction.

During the course of a geological survey of the Wellington district, the relation of the topography to the geological structure was found to be of interest, as was also the development of valley-in-valley formations. Observations were made in sufficient detail to make an account of the physiography worth while, even though the details are incomplete for some parts of the area. Heights were determined by aneroid, and have been checked wherever possible, but they must be regarded as approximate.

The town of Wellington is situated on the Central Western Slopes of New South Wales at the confluence of the Bell with the north-westerly flowing Macquarie River. It is about fifty miles (direct) from Orange in a direction slightly west of north and thirty miles south-east of Dubbo. The area which has been geologically mapped extends twenty-five miles northwards from a line joining Yeoval and Mumbil, and in all, includes nearly 500 square miles of country. It is not a physiographic unit in itself but forms part of the valley tract of the Macquarie River close to its emergence on to the Western Plains (Fig. 1).

The physiography of the Wellington district has not been discussed previously in any detail, although A. J. Matheson (1931) gave a brief summary of the topography and published a very generalised contour map covering about 150 square miles.

The geological map (Fig. 2) was prepared in collaboration with Miss E. M. Basnett, M.Sc., with whom most of the field work was carried out. I would like to acknowledge here the unfailing encouragement and valuable advice given me by Dr. W. R. Browne, whose suggestions have been of material assistance in elucidating the physiographic history.

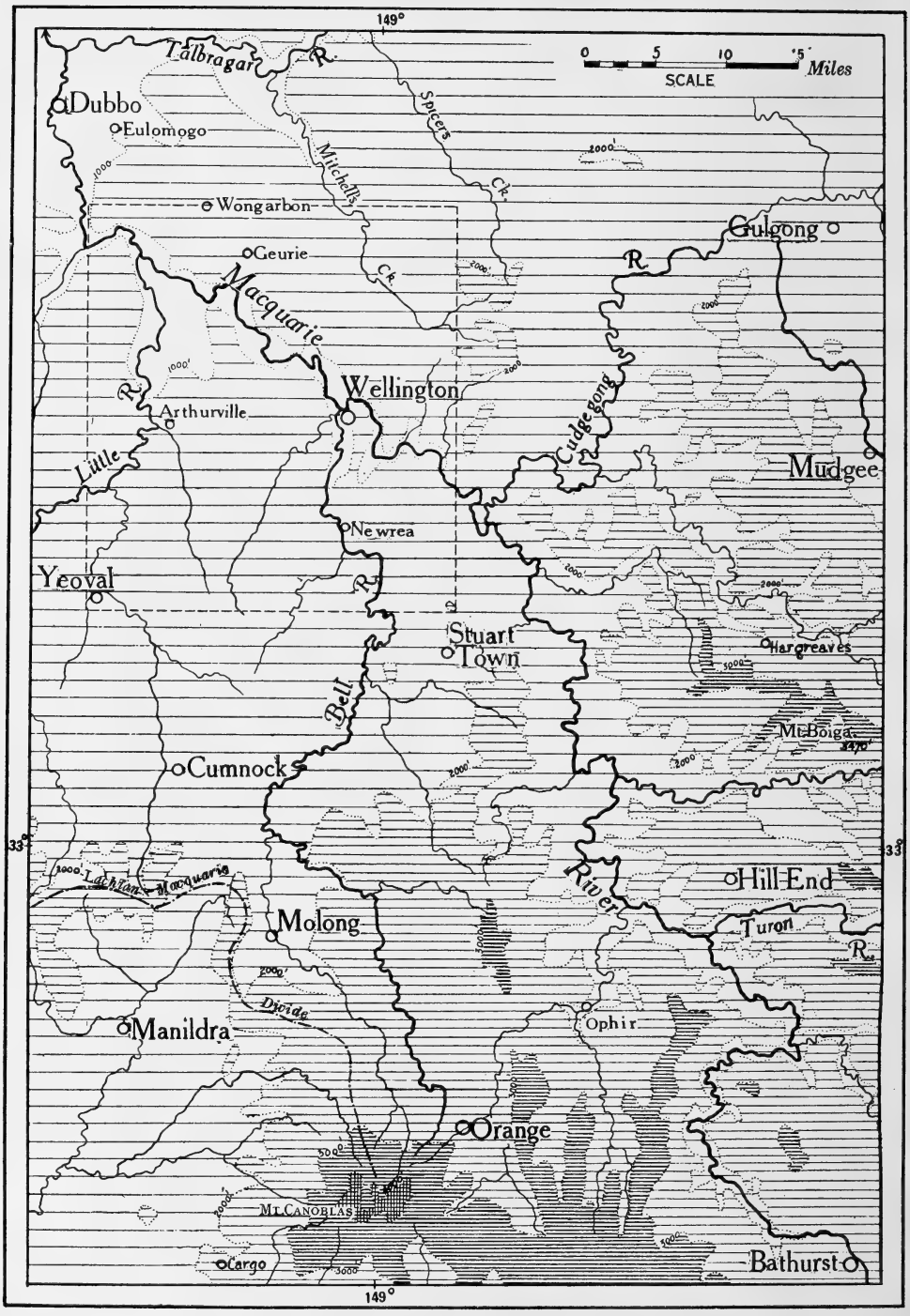

Fig. 1. Topographical map of part of the Macquarie River Drainage Basin. The area within the dashed lines is that dealt with in detail in this paper.

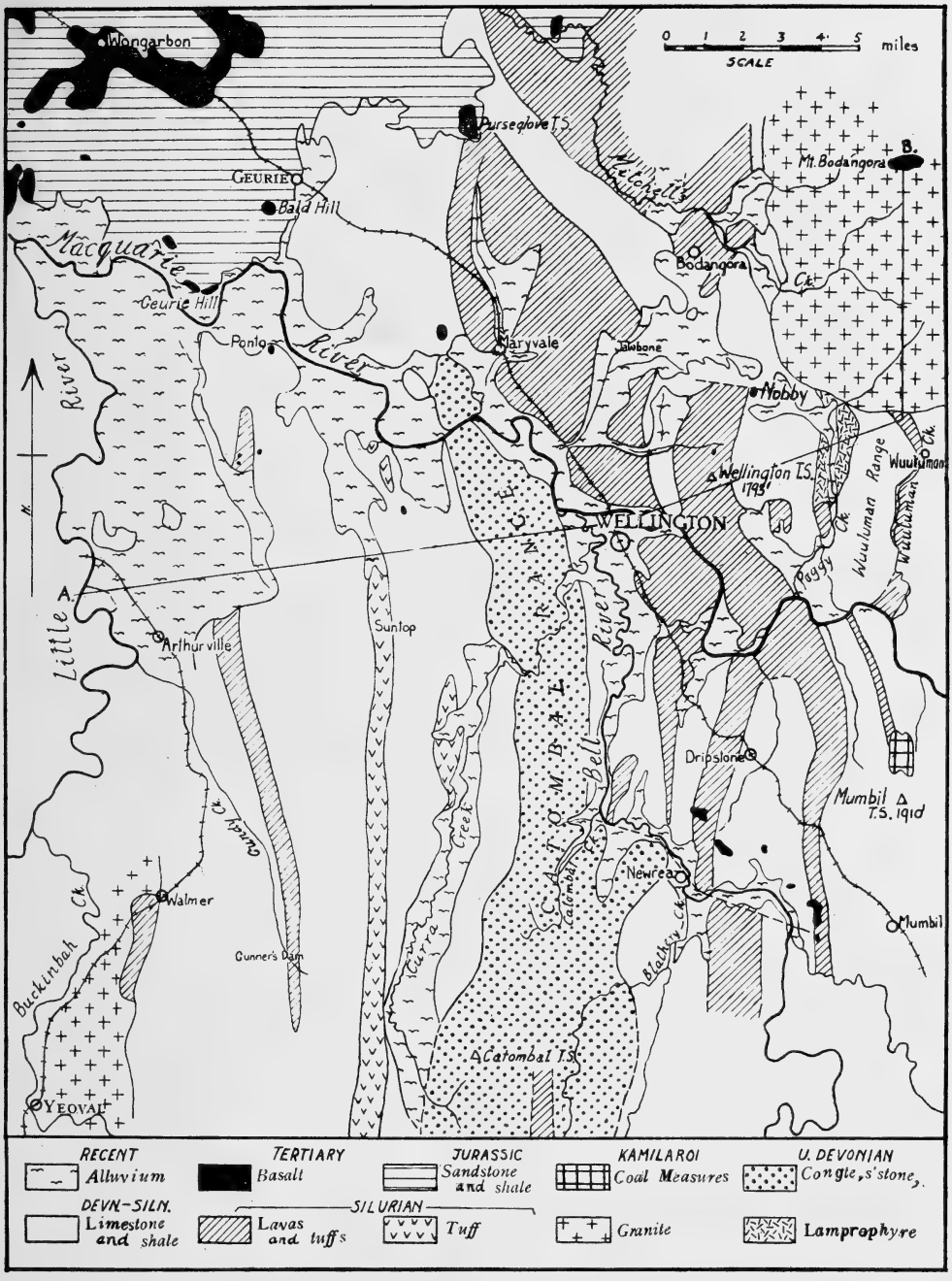

Fig. 2. Generalised geological map of the Wellington district. (Silurian and Middle Devonian sediments have been grouped together and Tertiary intrusions omitted.)

2. General Geology and Structure.

The greater part of the area mapped (Fig. 2) consists of limestones, shales, tuffs and volcanic rocks of Silurian age, overlain by Lower and Middle Devonian limestones and shales, and Upper Devonian sandstones, shales and conglomerates. These Middle Palæozoic rocks have been folded into a series of plunging anticlines and synclines which have a north-south trend and are intruded by the Yeoval and Wuuluman granites in the south-west and north-east respectively. Sills of augite-lamprophyre (Basnett, 1942) occur in Silurian slates to the west and north-west of Wuuluman.

The repetition of the volcanic and sedimentary stages by folding has produced more or less parallel bands of rock which differ in their resistance to erosion and so have formed alternating ridges and valleys whose direction conforms with the strike of the rocks. The synclinal formation of the Upper Devonian sediments of the Catombal Range and the folded Silurian strata of the Wuuluman Range have shown the greatest resistance and now form submeridional ranges nearly 2,000 ft. in height and 1,000 ft. above the present river levels (Pls. XIII, Fig. 2 ; XIV, Fig. 2). In the vicinity of Wellington T.S. and of Mumbil, the volcanic rocks reach almost to this height.

The north-western boundary of the area is delimited by Jurassic sandstones and shales which extend to the north-east and to the west and have a gentle dip to the north-west. Small plugs and dykes, probably of Tertiary age, are numerous, and patches of Tertiary basalt and of alluvium occur at different levels, overlying both Palæozoic and Jurassic strata.

3. Tertiary Basalt.

Scattered outcrops of basalt, probably of Tertiary age, occur throughout the district and are sometimes underlain by alluvial deposits. These few remnants of a once extensive basaltic sheet have preserved small portions of the pre-basaltic topography and from them the contour of the old land surface can be partly reconstructed.

The most elevated outcrop of basalt is that which caps Mt. Bodangora (Lincoln T.S.), a prominent landmark 2,500 ft. above sea level lying 13 miles north-east of Wellington. The base of the basalt is at 2,240 ft. approximately and below it lie 25 ft. of current-bedded sandstones and grits which are probably Jurassic but may be a later, pre-basaltic deposit. These sediments were deposited on an old surface of weathered granite which is 200 ft. above the highest parts of the present granitic surface. (Figs. 3, 7 ; Pl. XIV, Fig. 1.)

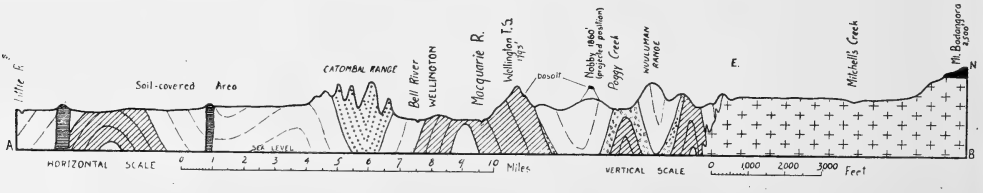

Fig. 3. Generalised section from the Little River through Wellington to Mt. Bodangora. $\frac{V}{H}=\frac{6}{1}$.

On the southern flank of the mountain a small conical hill is capped with basalt at 2,000 ft. As this basalt resembles the higher one petrologically, it is either a continuation of this flow at a lower level, or more probably, a plug filling the vent through which the basalt was extruded.

Thin cappings of basalt cover old alluvial deposits in the vicinity of and south-east from Newrea (Fig. 6). They form flat-topped hills along the eastern

margin of the present river valley, the base of the basalt being about 400 ft. above river-level and 1,480 ft. above sea-level (Pl. XIII, Fig. 3) and continue southwards towards Molong, where the outcrops are more continuous and appear to link up with basalts in the Orange district. Similar occurrences are to be found along the valley of the Macquarie River between Lewis Ponds Creek and the Cudgegong River (Fig. 4).

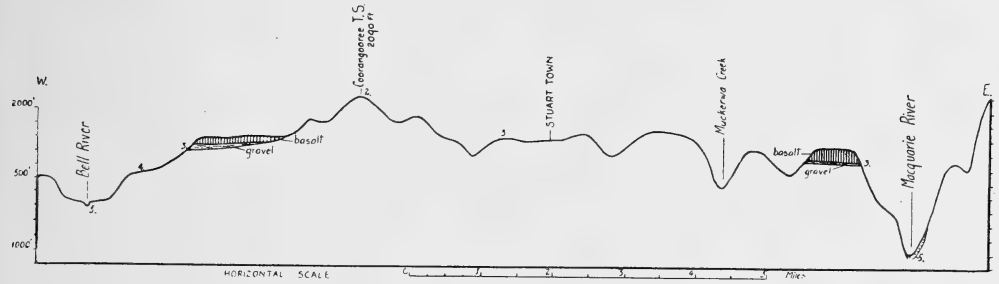

Fig. 4. Section from the Bell to the Macquarie River through Stuart Town showing basaltic terraces in the river valleys. (Drawn from information supplied by F. W. Booker, M.Sc.)

Small residuals occur three miles south of Ponto at about 1,200 ft. above sea-level and other cappings are to be found one and a quarter miles west of Maryvale (1,250 ft.), at Nobby, five miles north-east of Wellington at 1,860 ft., and two miles to the south-west of Nobby at 1,600 ft. The last two basalts are similar petrographically but not in field occurrence ; the latter is thin and lies on the shoulder of a hill which rises 150 ft. above it whilst Nobby is an isolated hill capped with 75 ft. of basalt (Fig. 3).

Basalt cappings occur at intervals along the Jurassic escarpment, as at Purseglove T.S., Geurie Bald Hill and Geurie Hill. At the first of these, 70 ft. of basalt overlies Jurassic sandstone at 1,500 ft. above sea-level, whilst Geurie Hill is at 1,250 ft. and 450 ft. above the Macquarie River, the total thickness of basalt being 225 ft. At Geurie Bald Hill (1,443 ft.) the base of the basalt lies above 1,200 ft. but is obscured by talus. Back from the margin of the Jurassic the outcrops of basalt become more continuous and are found at Wongarbon at 1,200 ft. and at Eulomogo at 1,100 ft. (Fig. 1).

4. Alluvial Deposits.

The alluvial deposits range in age from Tertiary to Recent ; some of the oldest underlie the basalt at Newrea and are 350 ft. above the alluvial flats (of the Bell River) ; they are as much as 60 ft. in thickness and consist of gold-bearing sands and gravels (Fig. 6 ; Pl. XIII, Fig. 3). Similar deposits occur along the valley of the Bell River towards Molong and also in the Macquarie River valley (Fig. 4). At Muckerwa Creek they consist of sand and quartz-gravels, some of which have become cemented with iron oxide (Jaquet, 1894).

About two miles west of Ponto in Por. 101, Par. Terrabella, quartz-gravels cap low hills on the eastern margin of the Little River alluvium. They have a cement of iron oxide and are between 150 and 200 ft. above the Macquarie River. Similar iron-cemented deposits occur between this locality and Dubbo and it is likely that they have been formed by the outpouring of basalt—now eroded away—over the gravels.

Younger alluvials than these are to be found on the north-eastern boundary of the town of Wellington on a terrace 1,000 ft. above sea-level and 50 ft. above the river, where they are quarried for use as road metal (Fig. 5 ; Pl. XIII, Fig. 1). Similar gravel-covered terraces occur on the Yeoval Rd., about two

miles from Wellington and also about four miles (direct) south-east from Ponto. Scattered gravels lie above the caves and on the lower terrace at Newrea (Fig. 6). All these deposits consist of pebbles which are usually not more than one inch in diameter and are chiefly quartz admixed and interbedded with coarse sand.

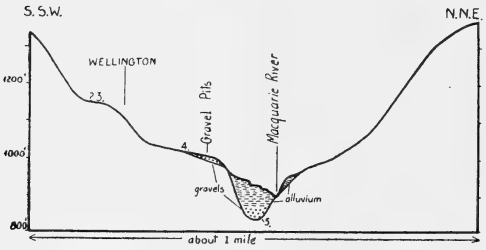

Fig. 5. Generalised section across the Macquarie River near Wellington, looking downstream. The configuration of the buried channel is hypothetical.

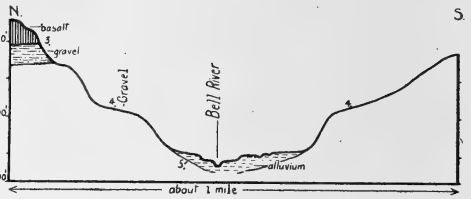

Fig. 6. Section across the valley of the Bell River a few miles above Newrea, looking upstream.

Thick deposits of bones and red earth occur in the Wellington Caves six miles south of the town in the valley of the Bell River. These are thickest in the topmost caverns and their mode of origin is uncertain, though there can be no doubt that they are younger than the caves which they fill. Thompson (1882) described the caves and suggested that they were filled from above. This infilling was probably caused by floods as well as by birds and other animals which frequented them.

Gravels which must be younger than those on the Wellington terrace and yet older than those of the present-day lie buried 100 ft. below the Macquarie River at Wellington, where they are being dredged for gold (Jones, 1935) (Fig. 5). They occur in an ancient channel of the Macquarie, of which there is evidence in other parts of the river course. Upstream near Stuart Town, Harper (1909) records an old channel 30 ft. below the present river bed, whilst downstream at Dubbo, gravels have been found 75 ft. below the river flats (Lloyd, 1934). At the Jawbone lead, east of Maryvale, auriferous gravels which were deposited by a tributary of the Macquarie River were worked to a depth of 60 ft. from the surface (Jones, 1935).

These buried river-deposits are not limited to the Macquarie as they have been recorded from the Lachlan River basin by E. C. Andrews (1910) thus : " Around Parkes old watercourses are found from 50 to 100 ft. below the present surface of the alluvium ; near Tichborne the old channels lie from 100 to 150 ft. below the present surface of the black-soil plain ; the famous South lead of Forbes has its channels as far below the surface as 210 ft."

The most recent of the alluvial deposits are those which form the present flood-plains and river-channels ; the former are fairly extensive and consist of grey loam whilst in the bed of the river coarse water-worn gravels occur.

5. Topography.

The town of Wellington (1,000 ft.) is situated in the valley of the Bell River at its junction with the Macquarie and is built on a terrace which forms a barrier as much as 100 ft. in height between the two rivers (Pl. XIII, Fig. 1).

The Bell River flats, which are two miles in width, are bounded on the west by the Catombal Range and extend southwards for about five miles (Pl. XIII, Fig. 2), whilst the alluvium of the Macquarie River continues northwards from the town towards Maryvale. The Catombal Range trends in a north-

north-westerly direction to the Macquarie River, north of which a ridge continues for about two miles and passes imperceptibly into the remnants of a former erosion-surface 1,250 ft. in height. Towards its northern limit the range, which is strongly dissected by insequent streams draining to the two main rivers, consists of a series of peaks, the chief of which, Mt. Arthur, has an altitude of 1,875 ft. and is 880 ft. above Wellington railway station.

The topography of the whole of the south-eastern part of the area has been strongly influenced by the strike of the Palæozoic rocks (Figs. 2, 7). Valleys carved from shale and limestone alternate with ranges of hills which consist either of Silurian volcanic rocks or of resistant sediments. The relief of the country varies from 300 to nearly 1,000 ft., increasing eastwards from the Bell River (Fig. 4).

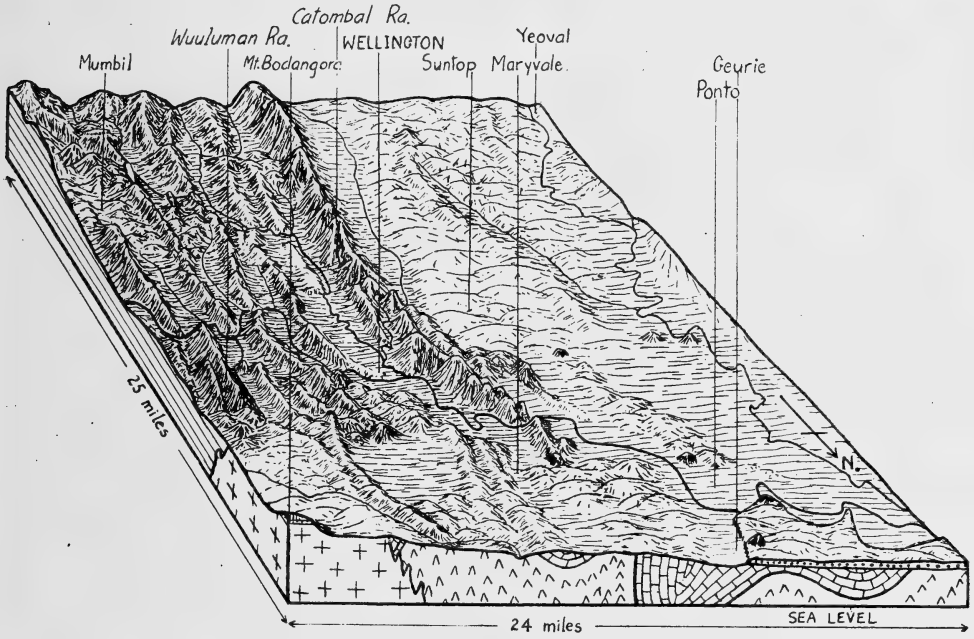

Fig. 7. Block diagram of the Wellington District. (See Fig. 2.) $\frac{V}{H} = \frac{6 \cdot 5}{1}$ approx.

The area between Yeoval and Bodangora is much more mature than this, and although the original trend of the hills has been retained in places the slopes are gradual and relief is usually between 50 and 100 ft. (Pl. XIV, Fig. 2). Outcrops are rare as the underlying rock has been covered with a thick mantle of reddish-brown soil probably derived in part from preceding surfaces of erosion. This soil is very suitable for wheat growing and resembles the " thick waste sheet of exceedingly gentle slope, often extending from the alluvium proper up to the very summits of the low hills which rise from the plains " of the Forbes-Parkes district (Andrews, 1910).

Along the courses of the Macquarie River and its tributaries alluvial flats have been formed varying in width according to the nature of the underlying rocks.

The Jurassic sandstones crop out as a low escarpment which rises above the Palæozoic basement. The base of the scarp rises to the north-east and falls to the west ; at Purseglove T.S. it is 1,500 ft. above sea-level, at Geurie 1,000 ft.

(150 ft. above the river), while at Geurie Hill it is almost at river-level. The Jurassic rocks form an undulating surface which extends towards Dubbo from Geurie, and also to the north ; near Geurie it is about 1,300 ft. but this elevation increases northwards and decreases to the west.

North-east of Wellington the Wuuluman granite forms an elevated area of small extent which rises at the margins to 2,000 ft. and slopes from 1,800 ft. in the south-east to 1,300 ft. near Bodangora, where Mitchell's Creek flows from it towards the Talbragar River. On its north-eastern edge (2,000 ft.) Mt. Bodangora rises to a height of 500 ft. (Figs. 1, 2, 7 ; Pl. XIV, Fig. 1).

6. Drainage System.

(1) *General.*

The Macquarie, known above Bathurst as the Fish River, rises to the south of Oberon, where the plateau is about 4,000 ft. above sea-level, and flows northwards towards Tarana, where it emerges from a deep " gorge " on to the so-called Bathurst Plains, across which it takes a west-north-west course to Bathurst. This broad valley has been carved from granite and at Bathurst the river (2,150 ft.) is about 1,000 ft. below the level of the Orange Plateau. A few miles to the west it enters another " gorge " through which it flows in a north-north-westerly direction to its junction with the Cudgegong River (Fig. 1), whence its general direction changes to the north-west as it flows through Wellington towards Dubbo. In this part of its tract the steep-walled valley gradually gives place to one of more gentle configuration and alluvial flats become more extensive. Between Geurie and Dubbo entrenchment within the Jurassic surface is evident, though to a depth no greater than 400 ft.

The gradients for these portions of the river's course are as follows : Oberon-Tarana, 27 ft. to 1 mile ; Tarana-Bathurst, 11 ft. to 1 mile ; between the Turon and Cudgegong Rivers, 9½ ft. to 1 mile (Harper, 1909) ; between the Cudgegong and Little Rivers, nearly 3 ft. to 1 mile.

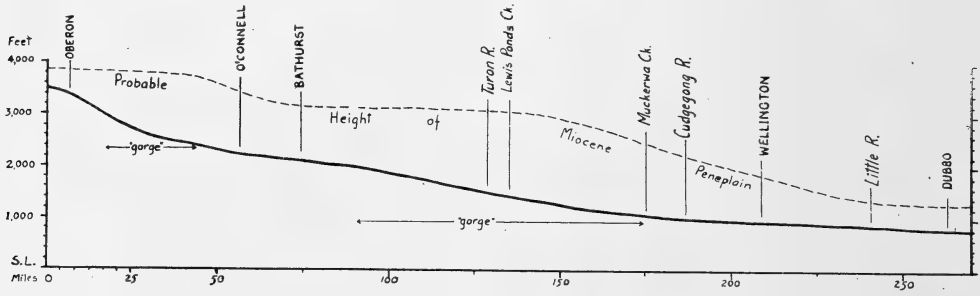

Fig. 8. Thalweg of the Macquarie River between Oberon and Wellington. The broken line indicates the probable height of the Miocene peneplain before erosion, in the vicinity of the river course.

Below Dubbo the Macquarie soon reaches the Western Plains, and of this part of its course H. G. McKinney (1885) writes as follows : " As the river reaches the plains and passes in a tortuous course towards the Darling, the rate of fall diminishes (2 ft. 6 in. per mile from Dubbo downwards) and the channel decreases in size till it reaches the Macquarie Marshes, where it divides into a number of creeks ; with a low discharge in the upper parts of the river the water disappears before it reaches the Marshes. In ordinary floods the diminished section of the channel obstructs the passage of the flood-water and forces a portion of it over the left or lower bank ; the remainder of the flood-water passes on to the Marshes, where it spreads out in a thin sheet over immense reed beds

and is there retained till it disappears by evaporation and absorption. In extraordinary floods only, does the Macquarie water reach the Darling ; on such occasions the floods escape over the left bank of the Macquarie in many places, the first being at Narromine, and flow in a series of creeks to the Bogan and thence to the Darling."

Between Wuuluman Creek and the Little River the Macquarie flows in a north-westerly direction and is fed by several tributaries, the Bell and Little Rivers being the only ones of importance (Fig. 2). Creeks which flow eastwards from the eastern margin of the Wuuluman granite reach the main stream by way of the Cudgegong River, and Mitchell's Creek, which rises in the granite, flows north-west to the Talbragar, which joins the Macquarie four miles below Dubbo.

The direction of flow of the Macquarie River in the Wellington area, as well as the structure of its valley, indicate that it is an entrenched consequent stream fed by tributaries of a subsequent character, these in turn having smaller insequent tributaries. In the less mature parts of the district the nature of the rocks and their structures have had an important bearing upon the direction of flow of both consequent and subsequent streams and upon the relative maturity of their valleys.

Owing to the extent of its catchment it is only during exceptionally dry summers that the Macquarie River ceases to flow at Wellington. The Bell, which has a more restricted drainage area (Fig. 1), is normally a small stream which may cease flowing for part of the summer, but waterholes remain and wells along its banks also yield a permanent supply of water.

Other watercourses, with the exception of Curra Creek, contain water only after heavy rain, as it is transported rapidly to the main stream.

(2) *Valley Form and its Relation to Geological Structure.*

(*a*) *The Macquarie River.* Below Wuuluman Creek the Macquarie River has the characteristics of a superimposed consequent stream as it meanders obliquely across the strike of the country towards its junction with the Little River (Fig. 2). The form of these meanders appears to have been influenced to some extent by the nature of the rocks and probably by jointing, as the river has repeatedly carved its way first along, and then across, the strike of the beds, so that in its north-westerly journey it proceeds in short distances to the west and longer distances to the north. Below its junction with the Little River, where it flows through the more homogeneous Jurassic rocks, the course of the flood-plain is more direct and the river meanders through it in a northerly direction to Dubbo.

In the eastern parts of the area where the river cuts its way through hardened slates and porphyry the valley-floor is narrow and the walls rise steeply from it to a height of 500 ft., but north-west of Wellington the flood-plain widens considerably along the strike of easily eroded sediments. The western wall of the valley is steep where the river course impinges on the Upper Devonian rocks of the Catombal Range, and when it cuts across the strike of these rocks the valley narrows suddenly. Once this barrier is passed, however, the flood-plain becomes extensive and the valley walls are low and gently sloping.

The accumulation of alluvium along the strike of the beds is probably due, not only to less resistance to erosion in this direction, but also to the fact that the hard rock downstream forms a barrier to the flood-waters, which deposit their silt behind it. The same effect is produced in the lower reaches of the Bell and Little Rivers and in less important tributaries by the flooded Macquarie which backs up the flood-waters of its confluents and so causes them to drop their burden of silt.

Throughout its course the river flows between banks of alluvium usually between 30 and 50 ft. in height and rock barriers occur at intervals along a bed of

sand and gravel. Terraces are developed in the banks and flood plain and small anabranches are common.

(*b*) *The Tributaries of the Macquarie.* Like that of the parent stream the tributary valleys vary according to the nature of the rocks in which they are cut. Many of them trend in a northerly or southerly direction and are separated by strike-ridges (Fig. 7). Where they join the Macquarie the alluvium is usually deep and extensive and the angle of confluence may be very acute; this is particularly the case with the Bell River where a long narrowing tongue of alluvium extends between the two rivers approaching their junction. The gradual slope of this tongue from 100 ft. above the river (Pl. XIII, Fig. 1) suggests that there has been a westerly migration of the junction from a position east of Wellington and two miles above its present locality. Matheson (1931) was also of this opinion. The same process has probably occurred with the Little River, which may have originally flowed into the Macquarie on the eastern boundary of its present alluvium (Fig. 2).

The Bell River, which has its source near Orange (Fig. 2), has a course much more accordant with the structure than has the Macquarie in the area studied (Fig. 2). From above Newrea it flows in a mature valley along a line of faulting towards the Catombal Range, against which it turns to the north, leaving the Upper Devonian on the west and carving its valley in the Middle Devonian and Silurian limestones. Its alluvial banks are from 15 to 20 ft. high, and terraces and anabranches occur on the flats.

Chief of the tributaries of the Bell is Curra Creek, which rises near Catombal T.S. and flows northwards along the strike of the Middle Devonian sediments on the western side of the Catombal Range (Pl. XIV, Fig. 2). Its valley here is wide and mature but at the Arthurville Road crossing, it bends suddenly to the south-east, then to the north and finally flows to the north-east through the range in a narrow, flat-floored but steep-walled valley till it reaches the alluvial flats of the Bell.

The peculiar course of this stream may be due to the capture of a north-flowing tributary by a stream which had cut back through the Catombal Range, the new creek subsequently becoming entrenched. This suggestion is borne out by the fact that water-worn gravels occur a few miles to the north of Suntop at a height of 1,300 ft. above sea-level and 220 ft. above the level of Curra Creek at the Arthurville Road crossing.

Mitchell's Creek meanders across the Wuuluman granite through banks of coarse sand studded with pink felspar crystals from the weathering of the porphyritic granite. Further downstream it flows through Silurian lavas and tuffs for more than ten miles before reaching the Jurassic sandstones. The volcanic rocks offer more resistance to erosion than does the granite and crop out along the banks and bed of the stream. The nature of its valley within the Jurassic has not been observed.

The northerly direction of flow of this stream suggests that its source may have lain somewhere near the southern limit of the old Jurassic cover. The sediments probably existed here as a thin mantle on the granite, at least until the outpouring of the Mt. Bodangora basalt, after which further erosion removed both basalt and Jurassic rocks, leaving the creek to become superimposed, in its upper reaches, on the underlying Palæozoic rocks.

One of the most interesting of the minor tributaries of the Macquarie River is Poggy Creek, which rises in the south of the Wuuluman granite and flows throughout its course in an alluvial channel between 15 and 20 feet deep. For two miles south of the granite it has carved a broad valley in the augite lamprophyre, an easily weathered rock, but where the volcanic series comes to the surface the creek is forced to flow through a gorge to the alluvium of the main

river (Fig. 2). Upstream from the gorge the wide flood-plain has well developed terraces probably due to the damming effect of the gorge.

A small intermittent creek with a narrow channel joins the Macquarie River in the flats about two miles north of Wellington. Its junction with the main stream has been effected through a resistant barrier of volcanic rock, in contrast to the upper part of its tract, which lies in a zone where easily eroded shale and limestone have been further weakened by intense folding and faulting. The resistant band has probably played some part in the damming back of the stream and the deposition of the wide sheet of alluvium which covers the gravels at Jawbone. The latter however indicate the presence of a more vigorous tributary 60 ft. below the present surface at a time when the Macquarie flowed through its deeper, more youthful valley.

The streams, both large and small, are entrenched in alluvium, but whereas the former have banks which are terraced and often slope gently, the small channels are usually narrow with almost vertical banks carved from soil or alluvium. The floors of these channels are often formed of soil with occasional boulders and many have undoubtedly been formed by the effect of heavy storms on ploughed fields and cleared land. Increased run-off due to clearing must also have caused entrenchment of existing small watercourses.

7. Erosion Surfaces.

Within the Wellington district there are remnants of what appear to be five surfaces of erosion, of which the three most recent are represented by valley-in-valley structures. Most of the levels can be seen to the east and south of Newrea, some ten miles to the south of Wellington, where remnants of the old valleys of the Bell River and its tributaries have been preserved. In the areas of more mature dissection the different erosion surfaces are sometimes difficult to define as they grade into one another.

In the Parkes-Forbes district which lies 60 miles to the south-west of Wellington and is in the Lachlan River drainage basin, Andrews (1910) has recorded " remnants of at least four of these old valley floors which are distinctly enclosed by the high and widely separated quartzitic and granitic walls of the main valley ". Though these have not been described in sufficient detail to permit of correlation with the Wellington levels, their existence suggests the probability of such a correlation with this and also with other districts. A section across the Macquarie River east of Orange shows definite valley-in-valley structures which have been compared with the Wellington surfaces (Fig. 9).

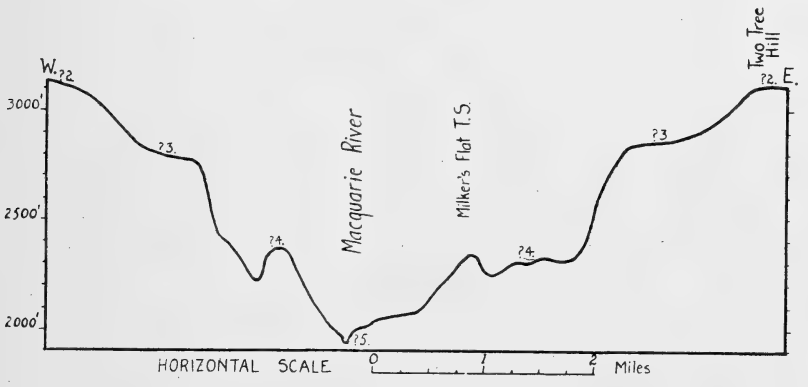

Fig. 9. Section across the Macquarie River Valley, 15 miles east of Orange, looking downstream. (Drawn from Orange Military Survey Map.)

The localities in which the various erosion surfaces have been best preserved are set out in Table 1 in order of decreasing age. The numbers have been referred to in the text and in some of the sections.

TABLE 1.

Remnants of Erosion Surfaces.

Surfaces.	Deposits.	Altitude.
	Feet.	Feet.
(1) Mt. Bodangora (Lincoln T.S.)	260 Basalt, 25 Gravels	2,500
(2) N. and E. margins of Wuuluman granite ..	—	2,000
Wuuluman Range	—	—
(3) Terrace above Bell R., E. of Newrea	20 Basalt, 60 Gravels	1,500
Upper terrace at Wellington	—	1,150
One mile W. of Maryvale..	15 Basalt	1,235
Three miles S. Ponto (Por. 130, Par. Ponto) ..	Basalt	1,200
Geurie Hill	225 Basalt, Gravels	1,250
Two miles W. Ponto (Por. 101, Par. Terrabella)	Ferruginous Gravels	1,050
Two miles N. of Suntop	Gravels	1,300
Nobby	75 Basalt	1,875
Two miles S.W. Nobby (Por. 92, Par. Nanima)	Basalt	1,600
Ponto-Walmer	—	1,300
(4) Lower terrace above Bell R., Newrea	Gravels	1,250
Apsley	—	1,100
Wellington terrace	Gravels	1,050
(5) Buried Macquarie valley at Wellington.. ..	Gravels	? 850

(1) At Mt. Bodangora sandstone and grit underlie a thick terraced deposit of basalt and represent what must once have been a continuous surface, but is now an isolated remnant standing 500 ft. above the surrounding country and 2,500 ft. above sea-level (Pl. XIV, Fig. 1). This surface is correlated with residuals rising above the Hargreaves-Hill End-Blue Mountain peneplain surface, i.e. with Mts. Hay, Tomah and King George and others.

(2) In the vicinity of Mt. Bodangora, particularly along the north-eastern and eastern margins of the Wuuluman granite, an old surface 2,000 ft. above sea-level is represented by hills of this elevation (Pl. XIV, Fig. 1). Further to the south the Wuuluman Range rises almost to this height, which is also approached by the higher points of the area, e.g. Mumbil T.S. (1,910 ft.), Mt. Arthur (1,875 ft.). This surface is believed to be an extension of the plateau which is so much in evidence in the Central Highlands, extending from Hargreaves to Orange and eastwards to the Blue Mountains (Fig. 1). Harper (1909) referred to this surface in its extension from the divide at Sunny Corner to Wellington as the Macquarie River Peneplain.

(3) Remnants of a wide valley floor about 500 ft. lower than surface (2) have been preserved along the Macquarie and Bell Rivers by patches of basalt which overlie alluvial material (Fig. 4). Alluvial cappings are to be seen at their best at Newrea and upstream along the Bell, where the base of the basalt is about 1,480 ft. or 400 ft. above river level (Pl. XIII, Fig. 3). Basalt-covered alluvial deposits occur along the Macquarie River between Muckerwa Creek and Lewis Ponds Creeks at heights comparable with those at Newrea.

Along the Bell River the cappings extend southwards towards Molong where the outcrops of basalt are more continuous and the depth of its dissection is much less. The basalt here appears to have filled a broad valley separated from the drainage of the Macquarie on the east and the Lachlan on the west by low

divides which now rise above the level of the valley basalts and are not themselves basalt-covered (verbal communication from D. Moye, B.Sc.). The broad valley extends southwards to Orange and merges gradually into the Orange Plateau.

At Wellington the public hospital and town reservoir are situated at 1,150 ft. on an old terrace (Pl. XIII, Fig. 1) between 200 and 250 ft. above the river (Fig. 5) ; the absence of gravels and basalt prevents a definite correlation, but it is comparable in elevation with other terraces included as remnants of this surface (Fig. 5).

Basalt cappings occur west of Maryvale, south of Ponto and at Geurie Hill. South of Geurie Hill and on the southern bank of the Macquarie River iron-cemented gravels occur 150 to 200 ft. above the river. It is thought that these were deposited by the river when surface (3) was in existence, and if this be so the gravel terraces between this locality and Dubbo must be a continuation of the old river bed.

Large water-worn pebbles of Upper Devonian quartzite have been found about two miles north of Suntop. They are 1,300 ft. above sea-level and more than 200 ft. above the height of Curra Creek at the Arthurville Road crossing.

Basalt occurs at Nobby, five miles north-east of Wellington at a little less than 1,800 ft. above sea-level, and another small patch is found two miles to the south-west at 1,600 ft. The latter is 300 ft. above the floor of a small valley and the country rises to nearly 1,800 ft. both to the north and south (Fig. 3). The Nobby flow may represent the higher part of the surface on which the basalt was poured out, and the lower level the old valley floor.

Between Yeoval and the Catombal Range surface (3) is probably represented by hills which rise above a lower undulating surface and are 1,300 to 1,400 ft. in the Suntop-Walmer area, rising fairly rapidly to the south. In the Geurie-Maryvale-Bodangora area, conditions are similar to those at Suntop and the different surfaces are usually obscure.

The basalt-covered valley floor which lies 500 ft. below the plateau level and 400 ft. above the river is comparable with the valley floor represented by basalt-covered alluvials at Bald Hills and Stewart's Mount, near Bathurst. Here, the gravels are between 700 and 400 ft. below the plateau and 300 to 600 ft. above the river. From Cargo, in the Lachlan River drainage basin, Andrews (1915) has described alluvial wash on hills 500 to 600 ft. below Orange and in places this wash is covered with basalt ; this also probably represents a stream course which existed during the formation of surface (3) at Wellington.

(4) At Newrea a terrace lower than the basaltic one and 150 to 200 ft. above the river has been much dissected but can be traced quite easily in places (Fig. 6 ; Pl. XIII, Fig. 3) and is sometimes capped with water-worn gravels. It can be followed along the valley of the Bell to Wellington and includes the Wellington Caves limestone belt ; at Apsley it is at 1,100 ft. and from there it can be followed down to the higher parts of the ridge on which the town of Wellington is situated. This ridge is capped with gravels and its greatest altitude is 1,050 ft. (Fig. 6 ; Pl. XIII, Fig. 1).

(5) The lowest valley floor of the Macquarie River is hidden beneath a deposit of alluvium which is 100 ft. thick at Wellington, 30 ft. at Stuart-Town and at least 75 ft. at Dubbo. There is therefore no visible record of the form of this valley except in those parts of it which are as yet unburied. These, taken in conjunction with the width of the present flood-plains, indicate that it was wide in some places and steep-sided and narrow in others, according to the nature of the underlying rock.

8. Age of Erosion Surfaces.

The allocation of ages to the erosion surfaces which have been described is a matter of some difficulty owing to the lack of fossil evidence. The scheme which has been adopted, admittedly conjectural, is set out in Table 2.

Table 2.

Physiographic History.

Age.	Events.	Type Locality.	Correlation.
? Eocene.	(1) Peneplain formed by streams flowing to the north-west. { Uplift (250 ft.). { Extrusion of basalt.	Mt. Bodangora, 2,250 ft. at base of basalt.	Mts. Hay, Tomah, etc. (Blue Mts.).
Oligo-Miocene.	(2) Development of extensive peneplain with residuals. Uplift (500 ft.)—in one or more stages.	Margins of Wuuluman granite, 2,000 ft.	Hargreaves-Hill End, Blue Mt. Plateaux.
Pliocene.	(3) Erosion of wide river valleys. { Extrusion of valley basalts. { Uplift (250 ft.). (4) Erosion of mature valleys. Uplift (200 ft.).	Upper terrace, Newrea, 1,500 ft. Lower terrace, Newrea, 1,250 ft.	Cargo, Bald Hills and Mt. Stewart (Bathurst). Parkes.
Pleistocene-Recent.	(5) Excavation of new river channels; filling of caves with bones and earth. Silting up of river channel to depth of 100 ft.	Channel 100 ft. below Macquarie River (800 ft. a.s.l.). Present flood plain.	Parkes.

A Miocene age is suggested for surface (2) on the basis of its correlation with the Hargreaves-Hill End Plateau and thence with the Blue Mountain Plateau. The latter is considered to be Miocene by physiographic writers such as E. C. Andrews (1910*a*) and C. A. Sussmilch (1937).

Surface (1), lying above the Miocene surface, is comparable with the residuals on the Blue Mountain Plateau, which are commonly believed to have been formed probably in Eocene time, partly covered with basalt, and uplifted possibly at the close of Eocene.

Taking the Oligocene and Miocene periods for the development of the peneplain of the Central Tablelands, the formation of valleys in this surface has been put into the Pliocene, though it may have commenced in the latter part of the Miocene. The basalt which lies in the wide valley of surface (3) covers leaf beds at Forest Reefs near Orange and a lower Pliocene age was suggested for these by Andrews (1914) on rather indefinite fossil evidence.

The erosion of the valleys of surface (4) has been assigned to the later Pliocene since it pre-dated the formation of the Wellington Caves and the deposits within them which probably range from Pleistocene to Recent (Anderson, 1933).

Andrews (1933) suggested that broad mature valleys were developed in the warped, basalt-filled valleys of eastern Australia before the Kosciusko movement, and this conclusion seems to agree with the late Pliocene age assigned to surface (4) at Wellington.

Deep leads similar to those of surface (5) have been described from Parkes by Andrews (1910*b*) who places them in the Pleistocene together with the *Diprotodon*-bearing black soil plains of the district.

9. Interpretation and History.

It is not known whether the Macquarie River existed on the oldest of the Tertiary land surfaces at Wellington, but it is quite probable that it flowed in a north to north-westerly direction across surface (1) to an inland lake during (?) Eocene time. Jensen (1907) believes that this and other north-westerly flowing rivers were formed as consequent streams on the uplifted Mesozoic surface.

The (?) Eocene plain was partly covered with basalt and was raised 200 ft. at the close of Eocene. During the long period of quiescence which followed during Oligocene and Miocene a new peneplain was formed with a few scattered remnants of the old surface rising above it. The Macquarie River certainly existed at this time and flowed in much the same direction as it does today. Between Bathurst and the Cudgegong River it followed the strike of the Palæozoic rocks, after which it changed direction and flowed as a consequent stream across the Wellington district. The river was fed by subsequent tributaries which flowed from north and south towards the parent stream and the whole system was in a state of extreme old age by the time the Miocene peneplanation was completed. The peneplain produced was so extensive that great stretches of it are still preserved in the highlands of eastern Australia.

Further uplifts and periods of stillstand at the close of Miocene and during Pliocene resulted in the successive entrenchment and widening of the streams, leaving a system of terrace levels to mark the positions of preceding valley floors.

The highest of these terraces at Newrea indicates that the peneplain was raised about 500 ft. at the close of the Miocene, following which valleys at least as much as five miles wide were eroded and to the east of Newrea the divide between the Bell and Macquarie was lowered to little more than 200 ft. The Catombal Range formed a ridge about 500 ft. high which was somewhat dissected in the north, while the country about Wellington T.S. was undulating with valleys 100 to 200 ft. deep, its general level being about 300 ft. below the plateau, which still existed to the east. West of the Catombal Range and in the Geurie-Bodangora area, wide, undulating and soil-covered expanses sloped gently towards the river, broken here and there by a low ridge or an isolated peak.

A further uplift of over 250 ft. in Middle Pliocene time was accompanied by an outpouring of basalt on the plateau, so extensive that it flowed down the valleys of the Bell and reached the Macquarie River by way of Lewis Ponds Creek. The flows reached at least to Newrea and to Stuart Town and at the same time extrusions probably occurred in the north-east of the region. Tributaries of the Lachlan River were also filled with basalt (Andrews, 1915) and the leaf beds at Forest Reefs were covered (Andrews, 1914).

In late Pliocene the rivers became entrenched, first of all into the basalt, most of which was removed in the process, and then into the old valley floor. Again there was a sufficient period of rest for the formation of mature valleys, not quite so wide as the previous ones. To the east of Wellington the meridional valleys were deepened, the strike ridges became more prominent and to the west and north a lower undulating surface was developed. At this time the topmost caverns of the Wellington Caves, destined to be filled with bones and earth, began to form.

The uplift which closed the Pliocene, and the subsequent entrenchment of the streams, left the upper caves (surface (4)) above river level but within easy reach of floods ; they probably had many openings to the surface, facilitating the entrance of materials and also of animals, while the lowest channel was being

excavated during the Pleistocene. Since the old river courses have been filled by alluvial deposits, the configuration of their lower portions is unknown.

The silting up of the Macquarie River was probably due to the same causes as resulted in the silting up of the Lachlan. Andrews (1915) suggests that this was caused " by a warping movement or one of irregular subsidence, by the decrease of stream action attendant on a decreasing rainfall, or again by the mature dissection of the hinterland ".

The movements of uplift which raised the Miocene peneplain to 3,000 ft. at Hargreaves caused an elevation to 2,000 ft. at Wellington and to less than 1,500 ft. at Dubbo (Fig. 8). This slope was produced by a series of differential uplifts which attained their maxima in the south-east and decreased rapidly to the north-west of Wellington. The total effect of the movement is comparable to the eastern monoclinal fold of the Blue Mountains except that in the west the slope is much more gentle and the uplift was more gradual.

The effect of the differential uplift on the Macquarie River has been profound. Each successive movement has caused rejuvenation, and upstream from the Cudgegong junction, uplift has been much greater than in the lower Macquarie, with the result that the river gradient changes fairly abruptly near Wellington (Fig. 8). Here also the river valley becomes mature and there is evidence of silting up of a deeper channel. Another important fact is that the terraces appear to converge downstream.

It is impossible to give an accurate estimate of the amount of each movement in this region, which is not far from the western hinge of uplift, but sufficient information is available to show that total uplift was distributed throughout the Tertiary period and that there was no culmination of movement at the close of the Tertiary as there was further to the east (Andrews, 1910*a*). The history of both the Wellington and Cargo districts may well be summarised in the words of E. C. Andrews after he had examined the Cargo Gold Field, west of Orange, in 1915 : " The elevation of the region proceeded intermittently, while the intervening periods of stable equilibrium and stream erosion were of great duration. This appears to have been the work of the earlier Tertiary and the great lesson of the Tertiary movements in this district is the slow and intermittent nature of the uplifts which culminated in the formation of the high plateaux, only after long, intervening periods of erosion."

10. Summary.

In the Wellington district, N.S.W., where Silurian and Devonian rocks are folded meridionally, part of the Macquarie River drainage system, during Tertiary and post-Tertiary times, produced two peneplains ; into the younger of these it was entrenched by separate movements of uplift giving rise to valley-in-valley formations. The structure of the rocks has determined the direction of flow of the subsequent tributaries and strike ridges have been developed. The Macquarie itself is a consequent river which originally flowed across the epi-Cretaceous land surface.

The history of previous land surfaces has been determined from the remnants of alluvial deposits and basalt flows. It is summarised in Table 2.

11. References.

Anderson, C., 1933. The Fossil Mammals of Australia. *Proc. Linn. Soc. N.S.W.*, **58**, ix.

Andrews, E. C., 1910*a*. The Geographical Unity of Eastern Australia in Late and Post-Tertiary Time. *J. Roy. Soc. N.S.W.*, **44**, 420.

Andrews, E. C., 1910*b*. The Forbes-Parkes Gold Field. *Geol. Surv. N.S.W. Min. Res.* 13.

Andrews, E. C., 1914. The Tertiary and Post-Tertiary History of New South Wales. *B.A.A.S. N.S.W. Hdbk.*, 1914, p. 518.

Andrews, E. C., 1915. The Cargo Gold Field. *Geol. Surv. N.S.W., Min. Res.* 19.

Andrews, E. C., 1933. Origin of Modern Mountain Ranges. *J. Roy. Soc. N.S.W.*, **67**, 251.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 1.

Fig. 2.

Harper, L. F., 1909. Notes on the Physiography and Geology of the North-Eastern Watershed of the Macquarie River. *Geol. Surv. N.S.W., Rec.* VIII, Pt. I, p. 321.
Jaquet, J. B., 1894. Report upon Auriferous Drifts on the Macquarie River. *Dept. Mines and Agriculture, N.S.W. Ann. Rept.*, p. 143.
Jensen, H. I., 1907. The Geology of the Warrumbungle Mountains. *Proc. Linn. Soc. N.S.W.*, **32**, 557.
Jones, L. J., 1935. Geological Survey of Wellington Gold Field. Progress Report. *Dept. Mines N.S.W., Ann. Rept.*, p. 76.
Lloyd, A. C., 1934. Geological Survey of the Dubbo District, with Special Reference to the Occurrence of Sub-Surface Water. *Geol. Surv. N.S.W. Ann. Rept.*, 1934, 84.
Matheson, A. J., 1931. The Geology of the Wellington District, with Special Reference to the Origin of the Upper Devonian Series. *J, Roy. Soc. N.S.W.*, **64**, 171.
McKinney, H. G., 1885. 1st Rept. Roy. Comm. Cons. Water, p. 61. (*Parl. Paper N.S.W.*)
Sussmilch, C. A., 1937. The Geological History of the Cainozoic Era in New South Wales. *Proc. Linn. Soc. N.S.W.*, **62**, viii.
Thompson, A. M., 1882. Exploration of the Caves and Rivers of New South Wales. (*Parl. Paper*), pp. 11, 12, 13.
Whitehouse, F. W., 1940. Studies in the Late Geological History of Queensland. *Univ. Qd. Papers, Dept. Geol.*, n.s., **2**, 1.

Description of Plates.

Plate XIII.

(1) A view of Wellington from the Yeoval Road (S.W. of the town). The town is built on a terrace (surface 4) on which gravel deposits occur at an altitude of 1,000 ft. Between this terrace and the hills behind it the Macquarie flows towards its junction with the Bell River, which meanders from right to left across the cultivated alluvial flats in the foreground. Pebbles from a gravel deposit similar to that at Wellington are visible in the immediate foreground. Wellington T.S. (1,793 ft.) is situated in the central distance.

(2) Looking S.S.W. up the valley of the Bell River from Wellington Common. In the background, on the Catombal Range, the boundary between cleared and uncleared land shows approximately the junction between Middle Devonian limestone and Upper Devonian sediments. Wellington Caves are situated in the low country shown about one inch from the left of the photograph.

(3) Looking to the N.W. across the Bell River valley, three miles east of Newrea, to a flat-topped hill on which basalt overlies alluvial deposits at an altitude of 1,480 ft. and 400 ft. above the river (surface 3). A lower terrace at about 1,250 ft. (surface 4) is shown by the long spur stretching towards the left from the basalt capping and also by shorter spurs in front of it. The river flows from east to west and an old position of the river bed is visible in the left foreground.

Plate XIV.

(1) Mt. Bodangora (2,500 ft.), from the south-eastern margin of the Wuuluman granite. The land slopes from 1,700 ft. in the foreground to 2,000 ft. above sea-level, the latter height extending on either side of the mountain (surface 2). The flat, terraced capping of basalt overlies about 20 ft. of fine grit which forms an escarpment at 2,220 ft. (surface 1).

(2) A south-easterly view of the Catombal Range from a few miles east of Gunner's Dam. The valley in the middle distance is that of the upper part of Curra Creek. This valley is lower than the undulating surface in the foreground which extends to the west, north and south of this locality (surface 3 ?).

UPPER ORDOVICIAN GRAPTOLITE HORIZONS IN THE YASS-JERRAWA DISTRICT, N.S.W.

By Kathleen Sherrard, M.Sc.

(With two text-figures and table.)

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Graptolites have been found in slate in a large number of localities to the east of Yass. The slate is of Upper Ordovician age and belongs to what has been called the Mundoonen Series (Sherrard, 1939). The graptolite-bearing localities are distributed about two centres, the first and larger being on both sides of the Yass River, between 12 and 16 miles upstream from Yass, and the second being about 1½ miles west of Jerrawa railway station (see maps, Figs. 1 and 2).

Through comparison of graptolites from all localities, it is possible to distinguish two different horizons in the graptolite-bearing beds. Some of the beds can be correlated with the lowest horizon among the Upper Ordovician beds in Victoria, which is designated Gisbornian, while others contain graptolites characteristic of the middle or Eastonian horizon (Harris and Thomas, 1938). The Bolindian or highest horizon has not been found.

I am indebted to Mr. R. A. Keble, F.G.S., of the National Museum, Melbourne; to Dr. D. E. Thomas, D.Sc., of the Geological Survey of Victoria; and to Dr. W. J. Harris, B.A., D.Sc., of Victoria, for their kindness in examining many of these graptolites and for the helpful advice they have given me. In no case, however, are they to be held responsible for any of the views expressed here. My thanks are also due to Dr. Ida Brown, of the Sydney University, for advice about the manuscript.

Table of Graptolites and Localities.

Graptolites found at each of the localities are shown in the accompanying table. All specimens are in the author's collection. Localities corresponding to the numbers in the table are as follows:

Locality 1.—Por. 24, Par. Morumbateman, on Yass-Gundaroo roadside, 100 yards west of 12th mile-post; in greyish shale, rarely blue-black on fresh surfaces, cross-jointed and iron stained.

Locality 2.—Por. 1, Par. Mundoonen, 200 yards north of Morumbateman Creek road junction with Yass-Gundaroo road; in fissile blue slate.

Locality 3.—Por. 152, Par. Manton; on top of river cliff about centre of portion, 50 yards north of Yass River; in bluish grey silicified slate.

Locality 4.—Por. 61, Par. Manton, eastern half; on bank rising from alluvial flood plain, in grey-blue slates with the close, fissile cleavage of roofing slates.

Locality 5.—Reserve No. 43134, Par. of Morumbateman, at waterfall, about half a mile north-west of junction between this reserve and Pors. 150 and 94, Par. of Morumbateman, in blue shale.

Locality 6.—Por. 31, Par. Morumbateman, near north-west corner, 50 yards south of Yass River; in silicified and shattered slate.

Table showing Graptolites occurring at various localities in the Yass-Jerrawa District.

Locality	1	2	3	4	5	7	9	10	11	13	14	16	17	21	23	24	26	27	28	29	31	32	33	34	35	36	37	39	40	41	50	51	52
Leptograptus flaccidus (Hall)	x								x	x										x		x					x	x			x		x
L. sp. indet.																																	
Dicellograptus elegans Carruthers				x															x		x				x		x					x
D. divaricatus Hall var. *rigidus* Lapworth				x																													
D. cf. *morrisi* Hopkinson		x		x															x						x								x
D. cf. *sextans* Hall		x	x	x																					x								
D. cf. *forchammeri* Geinitz		x																															
D. pumilus Lapworth				x				x											x														
D. cf. *pumilus* Lapw.																														x	x		
D. caduceus Lapworth										x									x		x												
D. affinus T. S. Hall			x																												x		
D. cf. *affinus* T. S. Hall															x				x														
D. sp. indet.	x									x																							
Dicranograptus furcatus Hall													x			x																	
D. cf. *furcatus* Hall		x																															
D. zic zac Lapworth										x											x								x				
D. cf. *zic zac* Lapworth														x														x					
D. hians T. S. Hall										x											x								x				
Climacograptus bicornis Hall	x									x		x	x			x						x	x	x	x		x			x			
C. missilis Keble and Harris	x	x		x																													
C. tubuliferus Lapworth				x											x				x							x	x				x		
C. cf. *tubuliferus* Lapw.							x																					x					
C. caudatus Lapworth															x				x		x						x				x		
C. cf. *caudatus* Lapw.										x	x			x														x					
C. brevis Elles and Wood																x			x					x									
C. cf. *brevis* Elles and Wood													x																				
C. cf. *minimus* (Carruthers)																			x												x		
C. sp. indet.																		x															
Diplograptus (*Orthograptus*) *calcaratus* Lapworth	x	x								x		x										x								x			
D. (*O.*) *calcaratus* Lapw. var. *basilicus* Lapw.		x		x	x																												
D. (*O.*) cf. *calcaratus* Lapw.																			x						x						x		x
D. (*O.*) cf. *calcaratus* Lapw. var. *vulgatus* Lapw.																															x	x	
D. (*O.*) *truncatus* Lapw.																			x		x												
D. (*O.*) cf. *truncatus* Lapw.	x	x		x						x																							x
D. (*O.*) *truncatus* Lapw. var. *pauperatus* E. and W.																			x			x											
D. (*Glyptograptus*) cf. *teretiusculus* (Hisinger)										x																							
D. (*G.*) cf. *teretiusculus* (His.) var. *siccatus* E. and W.														x																			
D. (*Amplexograptus*) cf. *perexcavatus* Lapworth													x	x																			
Diplograptus sp. indet.			x			x	x		x		x			x	x		x						x				x		x				
Retiograptus yassensis Sherrard and Keble		x																															
Glossograptus hincksii Hopkinson																														x			
Cryptograptus tricornis (Carruthers)		x											x			x								x					x	x			
Lasiograptus (*Thysanograptus*) *harknessi* (Nicholson)		x											x			x								x		x			x	x			
Cf. *L.* (*T.*) *harknessi* (Nich.)																	x				x					x							
Cf. *L.* (*T.*) *retusus* (Lapworth)													x																				
L. sp. indet.																			x														

Indeterminate graptolite fragments occur at Localities 6, 8, 12, 18, 19, 20, 22, 25, 30, 42, 43, and 53.

Locality 7.—Por. 126, Par. Morumbateman, on timbered ridge, about half a mile west-south-west of north-east corner post of portion in silicified slate, almost chert.

Locality 8.—Por. 126, Par. Morumbateman, on timbered ridge half a mile south of locality 7, in chert.

Locality 9.—Por. 126, Par. Morumbateman, on timbered ridge, a quarter of a mile west of north-west corner post of Por. 93 in compressed and weathered slate.

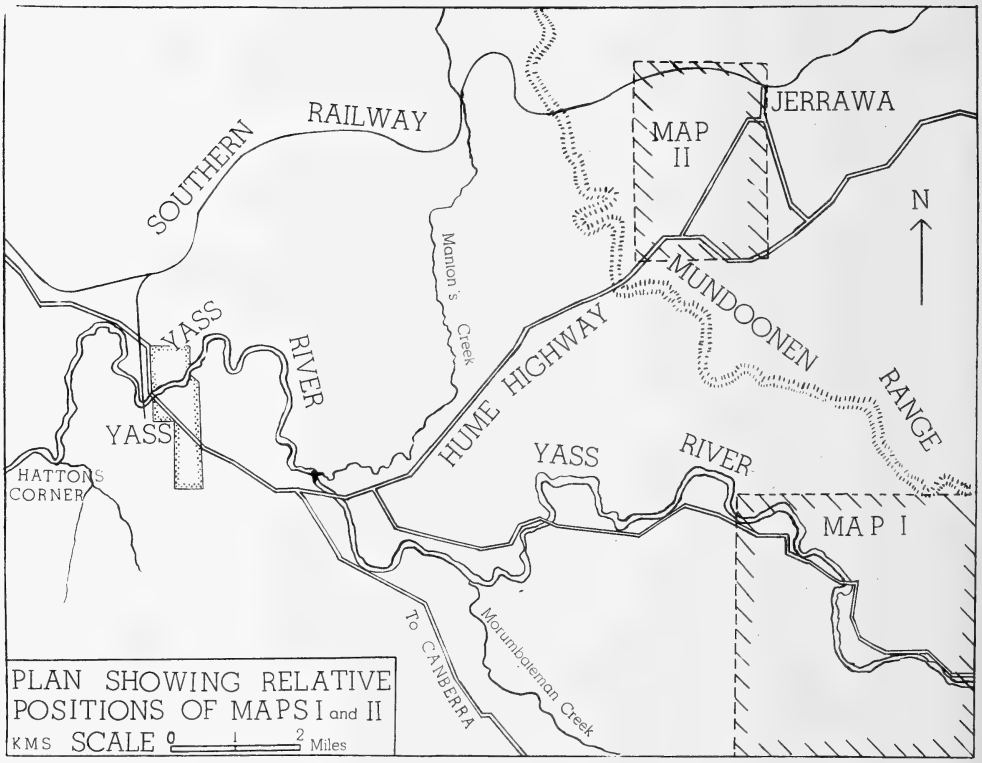


Fig. 1.

Locality plan showing relative positions of Maps I and II.

Locality 10.—Reserve 43134, Par. Morumbateman, in dry creek bed, nearly a mile west of north-east corner of reserve ; in silicified grey slate.

Locality 11.—Por. 81, Par. Mundoonen, west fence near north-west corner on south slope above creek, in blue fissile slate, rather weathered.

Locality 12.—Por. 158, Par. Mundoonen, in panhandle of portion beside north-west corner of Por. 81, Par. Mundoonen ; in grey mudstone.

Locality 13.—Por. 81, Par. Mundoonen, south-west quadrant in bluish-grey shale, good cleavage.

Locality 14.—Por. 110, Par. Mundoonen, 150 yards west of south-west corner post of Por. 81, in silicified slate overlying chert.

Locality 16.—Por. 80, Par. Mundoonen, top of ridge above Corrigan's Creek, on north boundary of portion ; blue-grey slate, silicified and weathered.

Locality 17.—Por. 80, Par. Mundoonen, 100 yards north of Corrigan's Creek, nearly 200 feet lower in elevation than locality 16.

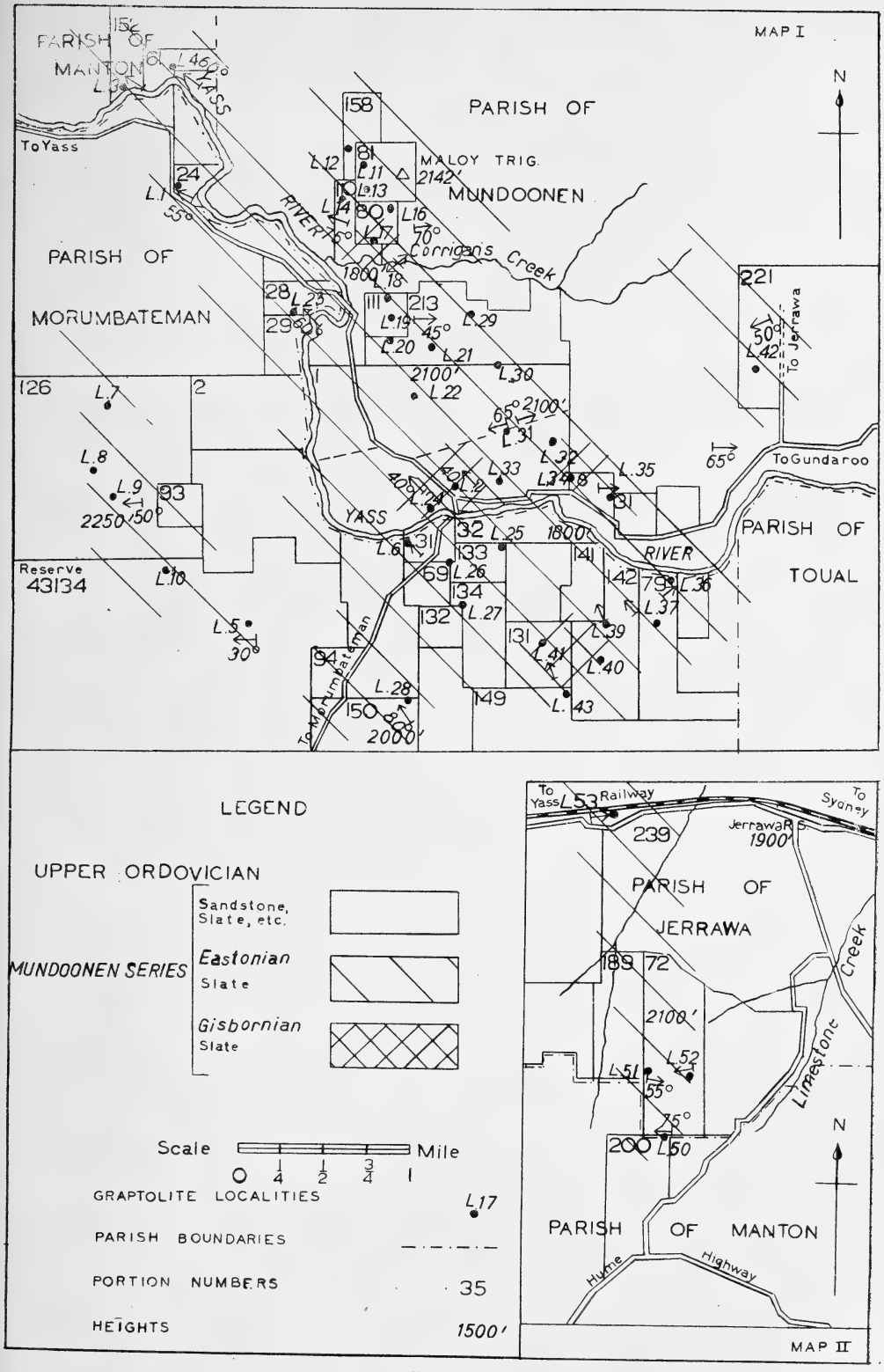


Fig. 2.
Map I. Geological sketch-map of the Yass River District.
Map II. Geological sketch-map of the Jerrawa District.

Locality 18.—Por. 111, Par. Mundoonen.

Locality 19.—Por. 111, Par. Mundoonen.

Locality 20.—Por. 213, Par. Mundoonen, just south of Por. 111.

Locality 21.—Por. 213, Par. Mundoonen, 200 yards south-east of south-east corner post of Por. 111 ; in highly silicified slate.

Locality 22.—Por. 1, Par. Mundoonen, 100 yards south of Por. 213 and 300 yards east of road.

Locality 23.—Por. 28, Par. Morumbateman, 300 yards south of road and 100 yards west of river, in creek ; poorly preserved in shale.

Locality 24.—Por. 1, Par. Mundoonen, across Yass River from Por. 31, Par. Morumbateman, and close to ford across river on Morumbateman Creek road ; in dense blue-black shale, fossils preserved in silvery chitin, very small forms, few more than one centimetre in length.

Locality 25.—Pors. 32 and 133, Par. Morumbateman, eastern margin.

Locality 26.—Pors. 69 and south-east 31, Par. Morumbateman, in blue slate.

Locality 27.—Por. 132, Par. Morumbateman, south-east of north-west corner post, in compressed blue slate.

Locality 28.—Por. 150, Par. Morumbateman, along north fence, 600 yards east of road, on top of ridge, in blue-grey slate.

Locality 29.—Por. 213, Par. Mundoonen, on ridge, about 600 yards south of Corrigan's Creek and two-thirds of a mile east of Yass-Gundaroo road, in blue silicified slate.

Locality 30.—Boundary of Pors. 1 and 213, Par. Mundoonen, about half a mile west of east fence of Por. 213.

Locality 31.—Por. 1, Par. Mundoonen, on ridge on diagonal fence through portion about 500 yards west of east fence of portion, in blue slate.

Locality 32.—Por. 1, Par. Mundoonen, 400 yards east-south-east of ridge end where is Locality 31, and 150 feet lower in elevation than 31, in blue-black shales.

Locality 33.—Por. 1, Par. Mundoonen, in small quarry, 150 yards north of Yass-Gundaroo road, slightly east of 15th mile post in blue-grey slate.

Locality 34.—Boundary between Pors. 1 and 8, Par. Mundoonen, about 150 yards north of Yass-Gundaroo road, near small waterfall, in dense blue-black shaly slate, all fossils small, seldom 2 cms. in length.

Locality 35.—Boundary between Pors. 8 and 31, Par. Mundoonen, 250 yards north of Yass-Gundaroo road, in weathered grey-blue slates.

Locality 36.—Por. 79, Par. Morumbateman, north-east corner, 100 yards south of river, poorly preserved in siliceous slate.

Locality 37.—Por. 79, Par. Morumbateman, in gorge, about centre of portion, 300 yards south of river, in siliceous slate, poorly preserved.

Locality 39.—Por. 142, Par. Morumbateman, at south-east corner of Por. 141, poorly preserved in silicified slate.

Locality 40.—Por. 142, Par. Morumbateman, 150 yards east of Por. 131, boundary, in slightly silicified blue slate.

Locality 41.—Por. 131, Par. Morumbateman, on bridle track to Toual, 300 yards west of fence of Por. 141, preserved in highly silicified slate.

Locality 42.—Por. 221, Par. Mundoonen, on ridge west of road to Jerrawa about half a mile north of Yass-Gundaroo road, in highly compressed slate, much weathered.

Locality 43.—Corner Pors. 131, 142 and 149, Par. Morumbateman.

Locality 50.—Boundary of Por. 200, Par. Manton, and Por. 72, Par. Jerrawa, on ridge, 500 yards west of west road from Jerrawa railway station to Hume Highway, in greyish-blue slate.

Locality 51.—Por. 72, Par. Jerrawa, near south-east corner of Por. 189.

Locality 52.—Por. 72, Par. Jerrawa, on top of ridge, about 400 yards east of junction between Pors. 189 and 203, poorly preserved in blue-grey slate.

Locality 53.—Por. 239, Par. Jerrawa. in low railway cutting, immediately east of road crossing to Needles Trig. station.

Horizons in the Upper Ordovician.

The table shows that the graptolite bearing localities fall into two distinct horizons. The beds at localities 17, 24 and 34 characterised by such forms as *Lasiograptus harknessi* (Nich.), *Cryptograptus tricornis* Carr., and *Climacograptus bicornis* Hall can be correlated with the Gisbornian (perhaps high in that horizon) of the Upper Ordovician as defined by Harris and Thomas (1938) for rocks in Victoria. The Gisbornian includes the zones of *Nemagraptus gracilis* and *Climacograptus peltifer.*

The graptolites of the beds at these localities are all small, none larger than 2 cms. in length. They are fairly well preserved as silvery, chitinous films on dense blue-black slates. The localities where they occur are all on or about river level, that is about 1,800 to 1,850 feet above sea-level, and their exposure is due to the erosive action of the Yass River and its tributaries, which have worked down through the centre of the anticline into which the Mundoonen series is folded (Sherrard, 1939). Localities 4, 23 and 36, for instance, are also near the level of the Yass River, but they occur at some distance from the central fold axis of the anticline, and are hence in higher beds and forms characteristic of the Gisbornian do not occur in these latter localities.

The rocks at localities 1, 3, 4, 13, 23, 28, 31, 32, 37 and 50 characterised by such forms as *Dicellograptus elegans* Carr., *D. affinus* T. S. Hall, *Dicranograptus hians* T.S.H., *Climacograptus caudatus* Lapw., *C. tubuliferus* Lapw., *C. bicornis* Hall, with long, drooping spines, *Diplograptus calcaratus* Lapw. and its varieties, *D. truncatus* Lapw. and its varieties, *Leptograptus flaccidus* (Hall) can be correlated with the Eastonian of Victoria, which includes the zones of *Climacograptus wilsoni* and *Dicranograptus hians* (Harris and Thomas, 1938).

The graptolites in the beds with Eastonian affinities are large. At locality 13, *Diplograpti* up to 10 cms. long have been found, and at locality 16, a virgella of great length attached to the same genus. At locality 50, a *Diplograptus* of the *calcaratus* type 7 mm. wide was obtained, though distortion by compression may have taken place. *Climacograptus tubuliferus* with spines was obtained in locality 28. *Dicellograpti* with stipes 12 cms. long were found at locality 13. The best preserved forms occur at localities 4, 13, 31 and 32. Most of the localities in this horizon occur at about 2,000 feet above sea-level, that is, nearly 200 feet above the beds whose fossil contents have enabled their correlation with the Gisbornian.

Beds at localities 2, 40 and 41 contain forms characteristic of both Eastonian and Gisbornian and may be near the junction of the two horizons. The upturned edges of the beds which occur at locality 2, outcrop on a steeply sloping hillside, and may pass from one horizon up to the other. Localities 40 and 41 occur in an area which has been intersected by quartz veins and may have been faulted.

Localities 5, 7, 8, 9 and 10 yielded but few forms, none well preserved. They occur in rugged, broken, heavily timbered country, and such as they are, are consistent with an Eastonian age.

All the forms found in the localities in the Jerrawa area, localities 50 to 53, can be referred to the Eastonian.

References.

Elles, G. L., 1925. *Geol. Mag.*, **62**, 337.
Elles, G. L., and Wood, E. M. R., 1903–08. *Mon. Pal. Soc.*, 57–62.
Harris, W. J., and Thomas, D. E., 1938. *Min. Geol. J. Dept. Mines Vict.*, **1**, 62.
Sherrard, K., 1939. *Proc. Linn. Soc. N.S.W.*, **64**, 577.
Sherrard, K., and Keble, R. A., 1937. *Proc. Linn. Soc. N.S.W.*, **62**, 303.

PERMIAN BRYOZOA OF EASTERN AUSTRALIA.

Part III. Batostomellidæ and Fenestrellinidæ from Queensland, New South Wales, and Tasmania.

By Joan M. Crockford, M.Sc.

(With Plate XV and two text-figures.)

Manuscript received, November 16, 1942. Read, December 2, 1942.

Summary.

Fourteen species of Bryozoa belonging to the Batostomellidæ and Fenestrellinidæ are recorded or described from localities in the Permian of Queensland, New South Wales, and Tasmania; of these species six are described as new.

Introduction.

The species of Bryozoa described occur in the Upper Marine Series of the Hunter River District and the South Coast of New South Wales, the Lower Marine Series of the Hunter River District, and the Permian of central Queensland and Tasmania. The following species are described:

Order Trepostomata.

Family **Batostomellidæ.**

	Page
Dyscritella restis sp. nov.	259
Dyscritella porosa sp. nov.	259
Stenopora gracilis (Dana), 1849	261
Stenopora nigris sp. nov.	263
Stenopora frondescens sp. nov.	264
Stenopora grantonensis sp. nov.	265

Order Cryptostomata.

Family **Fenestrellinidæ.**

	Page
Fenestrellina dispersa sp. nov.	265

Seven species are recorded from additional localities; one of these (*Fenestrellina horologia* (Bretnall)) has not previously been known to occur in eastern Australia.

Thin sections of specimens of some of the species described were lent for comparison by the Australian Museum; an impression of the surface of the lectotype of *Stenopora gracilis* (Dana), used for comparison with material from the type locality, was sent by Dr. R. S. Bassler; records of the occurrence of three species in the Permian of Queensland are made with the permission of Shell (Queensland) Development Pty. Ltd.; specimens from the Upper Marine Series near Cessnock were collected by Mr. A. H. Voisey. My thanks are due to Dr. Ida Brown for the help she has given me during the preparation of this paper, and for a number of the specimens described, which she collected in Tasmania.

This work was commenced during the tenure of a Science Research Scholarship at the University of Sydney.

Catalogue numbers of specimens, except where it is otherwise stated, refer to specimens in the museum of the Department of Geology, University of Sydney.

Description of Species.

Genus **Dyscritella** Girty, 1911.

Dyscritella Girty, 1911, 193 ; *Dyscritella* Girty, Lee, 1912, 151 ; Bassler, 1941, 178.

Genotype: Dyscritella robusta Girty, 1911.

Zoarium ramose or incrusting, usually with smooth maculæ ; zoœcia tubular, without diaphragms ; zoœcial walls thin in the axial and evenly thickened in the mature regions ; apertures oval or rounded ; mesopores numerous, usually aggregated at intervals to form maculæ ; acanthopores abundant, frequently in two series.

Dyscritella restis sp. nov.

Plate XV, fig. 9 ; Text-fig. 2A, B.

Holotype: 2448. *Occurrence:* Allandale Stage, Lower Marine Series, above Eurydesma conglomerate, railway cutting east of Allandale Station ; and Por. 34, Par. Middlehope, near Eelah Rd. crossing of North Coast Railway.

Ramose Dyscritella, *with large, not numerous acanthopores, and mesopores about equal in number to the apertures.*

The zoarium is ramose with cylindrical branches from about 1·2 to 1·8 mm. in diameter—the branches of most specimens from the type locality are flattened and appear to be of greater width ; smooth maculæ about 1 mm. in diameter and composed of aggregations of mesopores are rarely developed. The apertures are elliptical, and arranged in irregular diagonal rows ; they are 0·24 to 0·41 mm. long, and 0·14 to 0·21 mm. wide ; about 10 occur in 10 mm. longitudinally. The rims of the apertures may be slightly raised, so that the interspaces between them may be rounded or slightly concave. The acanthopores are in two series ; there are usually five or six large acanthopores around each aperture, but from four to eight may occur, and a few very small acanthopores also occur. Mesopores are about equal in number to the apertures ; they are rounded or oval, 0·03 to 0·2 mm. long, and 0·03 to 0·1 mm. wide.

The radius of the mature zone is 0·3 to 0·35 mm. ; the bend of the zoœcia from the axial to the mature zone is at an angle of 15° to 35°. The zoœcial walls are very thin in the axial region, but they are evenly thickened in the mature region to a width of up to 0·13 mm. between adjacent, and 0·25 mm. between consecutive, zoœcia. No diaphragms are developed in either zoœcia or mesopores.

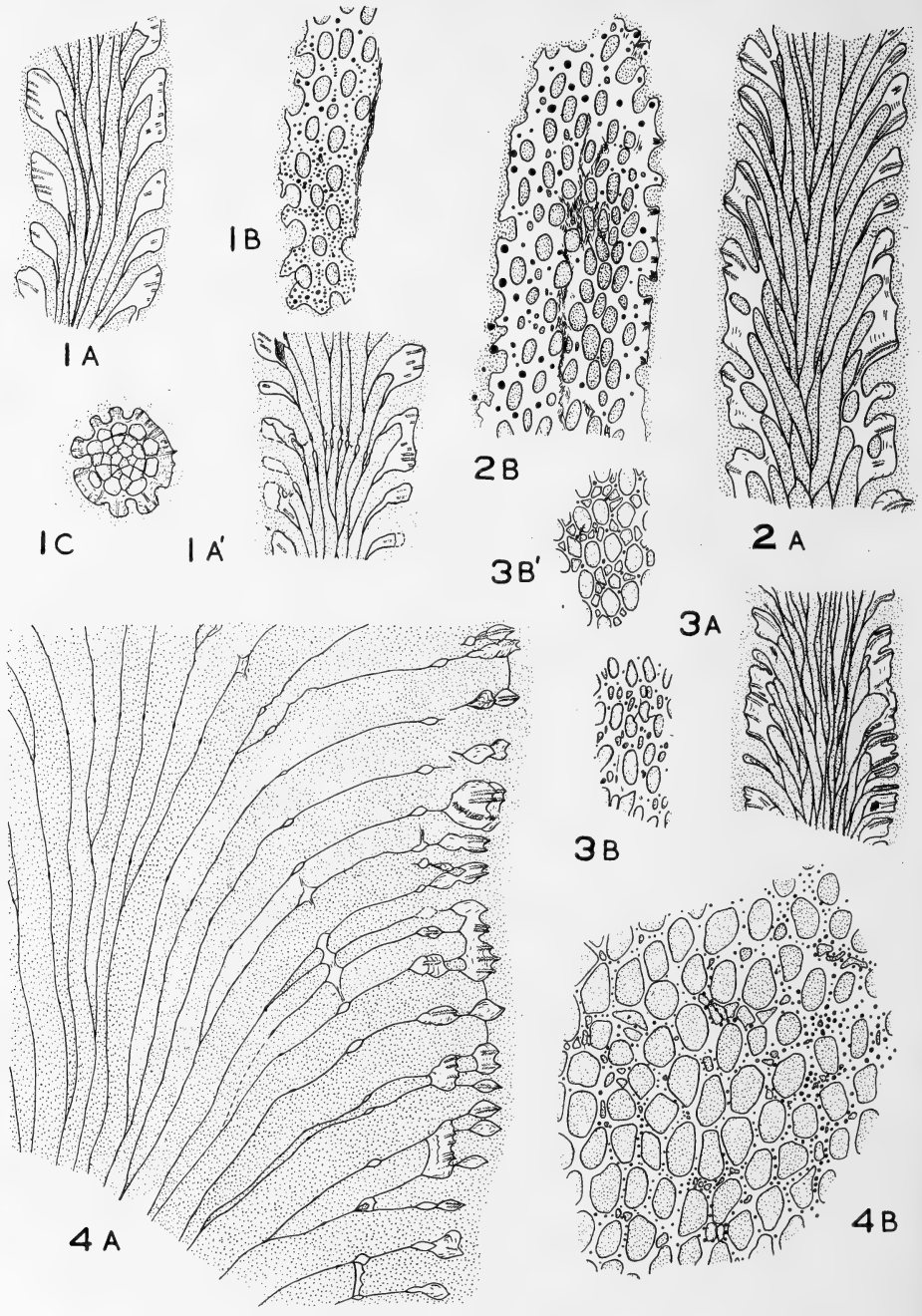
Dyscritella porosa sp. nov.

Plate XV, fig. 8 ; Text-fig. 3A-C.

Holotype: 3402. *Occurrence:* Allandale Stage, Lower Marine Series ; Jackson's Hill, Por. 132, Par. Pokolbin.

Ramose Dyscritella, *with abundant acanthopores and mesopores.*

The zoarium is ramose, consisting of cylindrical branches, usually between 1·5 and 1·75 mm. wide, but which broaden considerably before bifurcation, which occurs at intervals of about 7 mm. ; the angle between the branches after bifurcation is about 50°. The apertures are elliptical, 0·29 to 0·38 mm. long and about 0·2 mm. wide ; they are irregularly arranged, and are almost completely separated by numerous small, angular mesopores, up to about 0·17 mm.



(A. Vertical section. B. Tangential section. C. Transverse section.)

Fig. 1.—*Stenopora grantonensis* sp. nov. A′, vertical section, with the axial region crossed by an arcuate zone of thickening, here composed of two distinct rows of monilæ. (Specimen 2446.) ×10.

Fig. 2.—*Dyscritella restis* sp. nov. (Specimen 3400*a*, *b*.) (The width of the zoarium has been increased by compression of the specimens.) ×10.

Fig. 3.—*Dyscritella porosa* sp. nov. B. Tangential section, showing the mesopores near the base of the mature zone. B′. Surface of the zoarium, showing mesopores (B′, holotype; A, B. Specimen 3403*a*, *b*). ×10.

Fig. 4.—*Stenopora frondescens* sp. nov. (Holotype.) ×10.

in length ; about 10 apertures occur in 10 mm. longitudinally. Acanthopores are fairly numerous ; as many as eleven, but generally less than six, surround each aperture ; they are rather blunt, and project only slightly above the surface. Neither monticules nor maculæ were seen.

The zoœcia are very thin-walled in the axial zone but the walls in the mature zone are evenly thickened to a width of 0·1 to 0·15 mm. ; the bend of the zoœcia from the axial to the mature zone is not very sharp. The radius of the mature zone is 0·24 to 0·35 mm. No diaphragms are shown in either zoœcia or mesopores.

Genus **Stenopora** Lonsdale, 1844.

Stenopora Lonsdale, 1844, 178 ; *Stenopora* Lonsdale, Lonsdale, 1845, 262 ; Nicholson and Etheridge, 1886, 173 ; Etheridge, 1892, 32 ; Duncan, 1939, 242 ; Bassler, 1941, 173 ; Lee, 1912 [pars], 148 ; [non] *Stenopora* Lonsdale, Ulrich, 1890, 375, 436 ; Bassler, 1929, 54, 58.

Genotype : *Stenopora tasmaniensis* Lonsdale, 1844.

Synonym : *Ulrichotrypa* Bassler, 1929.

Zoarium massive, ramose, incrusting, laminar, or frondescent ; zoœcia tubular, thin-walled in the axial region, but with the walls in the mature region irregularly thickened (moniliform) ; diaphragms absent or extremely rare ; acanthopores well developed, generally large and very numerous, and commonly occurring in two series ; mesopores not tabulated, generally fewer in number than the zoœcia ; monticules or less often maculæ characteristically developed, except in some fine ramose species.

Lonsdale described (1844) and figured (1845) the genotype of *Stenopora* from the Permian of southern Tasmania ; Bassler (1941) has considered that *Ulrichotrypa* Bassler, 1929, is synonymous with *Stenopora*, and this course is followed here.

Stenopora gracilis (Dana), 1849.

Plate XV, figs. 1, 2 ; Text-fig. 5A-C.

Chætetes gracilis Dana, 1849, 712, t. 11, figs. 10, 10*a-c* ; [?] *Stenopora tasmaniensis* Lonsdale, Etheridge, 1892 [pars], 60 ; [non] *Stenopora tasmaniensis* Lonsdale, 1844, 178.

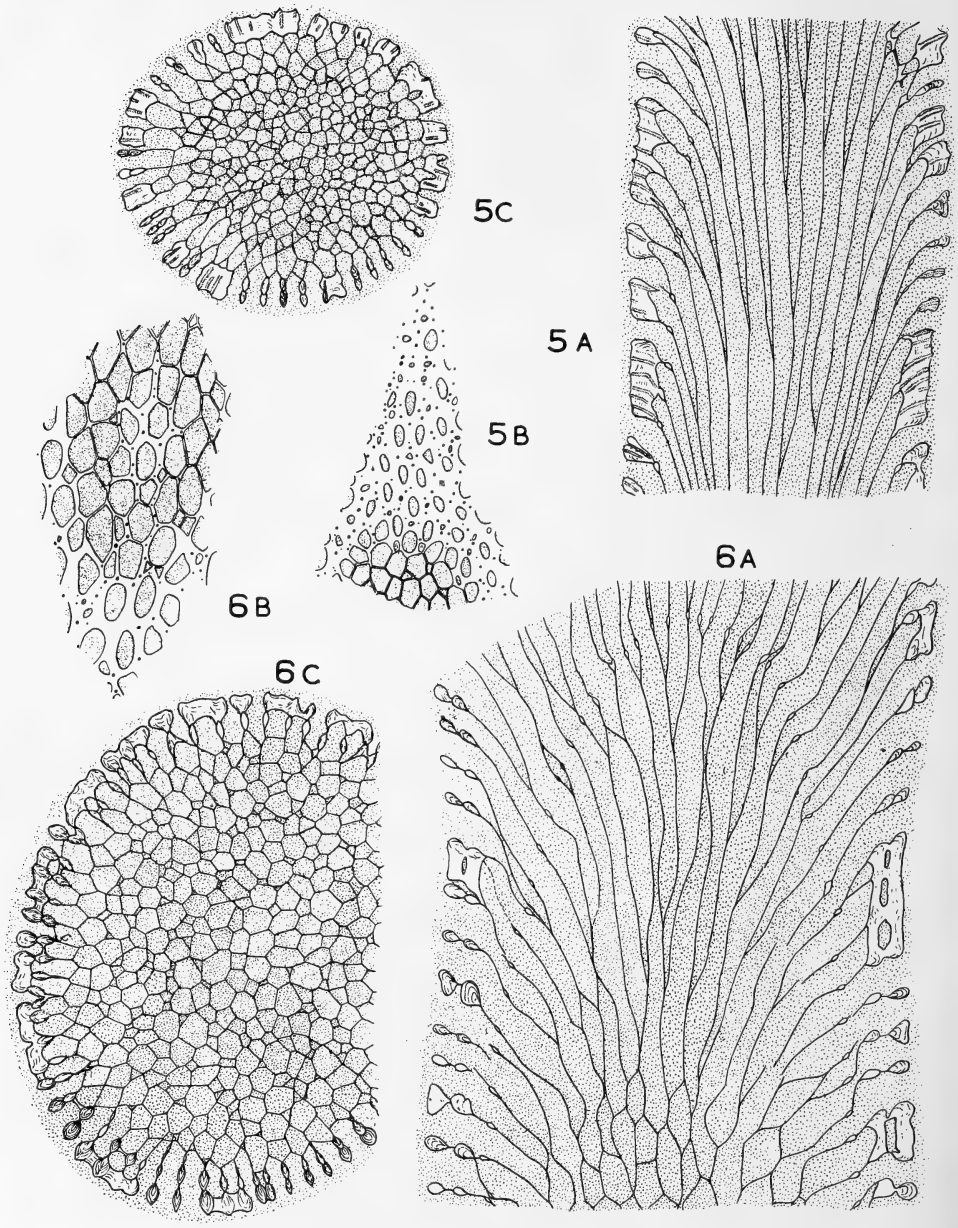
Lectotype (here chosen) : Specimen figured by Dana (1849, t. 10, figs. 10, 10*a-c*), which is with Dana's collection of fossils from Australia in the Smithsonian Institution, United States National Museum ; erroneously stated by Etheridge (1892, 2) to have been destroyed by fire.

Plastotype : Specimen 2417, Sydney University Collection.

Occurrences : The lectotype is from either the Westley Park Tuffs, Crinoidal Stage, Upper Marine Series, at Black Head, near Gerringong, N.S.W., or the Crinoidal Stage, Upper Marine Series, at Flagstaff Point, Wollongong, N.S.W. (Dana, 1849) ; *Stenopora gracilis* occurs also in the Westley Park Tuffs on the rock platform below Gerringong Trig. Station.

Fine, ramose Stenopora, *with a very narrow mature zone with two rows of monilæ, and a broad axial zone crossed by remote arcuate rows of monilæ ; mesopores not numerous ; acanthopores well developed ; diaphragms extremely rare ; small maculæ irregularly developed.*

The zoarium is ramose, attached to the substratum by a flattened circular base, about 13 mm. in diameter, from which a single cylindrical branch arises ; this bifurcates about 7 mm. above the base, and gives rise to a large ramose colony. The branches are cylindrical, 3·25 to 4·0 mm. in diameter, increasing



(A. Vertical section. B. Tangenital section. C. Transverse section.)

Fig. 5.—*Stenopora gracilis* (Dana). (Specimens 3406-3408.) ×10.
Fig. 6.—*Stenopora nigris* sp. nov. (Holotype.) ×10.

(*Camera lucida* diagrams.)

considerably in size immediately before branching, which occurs at very irregular intervals. The apertures are oval, 0·24 to 0·33 mm. long and 0·17 to 0·21 mm. wide; they are of normal size and shape near the base of the colony. The interspaces between the apertures are ridged or flat, with a single or double row of acanthopores, up to about 16 surrounding each aperture. Mesopores are far less abundant than the apertures; their openings are up to 0·14 mm. in length, but are generally very small; they are aggregated at irregular and rather infrequent intervals to form the maculæ. The apertures are irregularly arranged; about 11 occur in 5 mm. longitudinally, and from 35 to 40 occur around the circumference of a transverse section.

The mature zone comprises only about one-quarter of the radius, its width being 0·33 to 0·46 mm.; the bend of the zoœcia from the axial to the mature region is at an angle of about 40°, and the tubes meet the surface at almost a right angle. The zoœcia are thin-walled in the axial zone; they are oval in the mature zone, where the walls are thickened to a width of up to 0·27 mm. between two apertures longitudinally, or 0·16 mm. transversely. The walls are not strongly moniliform; two rows of thickening generally occur in the mature zone, but these often appear confluent; the outer row of monilæ is from half to three-quarters of the width of the mature zone. In addition remote arcuate rows of monilæ cross the axial zone at intervals of 5 to 15 mm. or more; each consists of a single row of thickening up to 0·15 mm. in length. The acanthopores are in two series; about eight large acanthopores, originating near the base of the mature zone, surround each aperture; the small acanthopores originate close to the surface—these are not usually shown in sections. Diaphragms are extremely rare; when developed they are thin, complete, and slightly curved backwards.

Remarks: Dana (1849) described this species from material collected at "Wollongong Point and Black Head, Illawarra" in 1839; his specimens are in the United States National Museum collections, but a gutta percha impression of the specimen which he figured has been compared with the specimens from Black Head and Wollongong, from which this revision has been made. Etheridge (1892, 60, 64) considered *Stenopora gracilis* possibly a synonym of *Stenopora tasmaniensis* Lonsdale, which is, however, a much larger form—Lonsdale gives the size of the branches as half an inch in diameter.

Stenopora nigris sp. nov.

Plate XV, fig. 7; Text-fig. 6A-C.

Stenopora tasmaniensis Lonsdale, Etheridge, 1892 [pars], 91, pl. VII, fig. 9; [non] *Stenopora tasmaniensis* Lonsdale, 1844, 178.

Holotype: 2444. *Occurrence:* Westley Park Tuffs, Crinoidal Stage, Upper Marine Series, at Black Head, near Gerringong.

Ramose Stenopora, *with smooth cylindrical branches 6 to 7 mm. in diameter; very narrow mature zone with two rows of monilæ, and broad axial zone crossed by remote arcuate rows of monilæ; mesopores few; acanthopores small, fairly abundant; diaphragms extremely rare.*

The zoarium is ramose, with a flattened oval base about 20 mm. long and 12 mm. wide, which gives rise to a single thick branch; this bifurcates about 1 cm. above the base, and the two thick branches formed by this bifurcation rapidly divide and give rise to a large ramose colony. The branches are cylindrical, 5·8 to 6·8 mm. in diameter; no monticules or maculæ are developed. The apertures are oval, 0·4 to 0·53 mm. long and 0·19 to 0·24 mm. wide, and the interspaces between them are flat or slightly rounded, with a single row of small acanthopores. The apertures are not regularly arranged, but about 9

occur in 5 mm. longitudinally, and from 54 to 64 are cut around the circumference of a transverse section. Small oval or rounded mesopores, up to 0·18 mm. long, occur rather infrequently.

The mature region is very narrow, comprising about one-fifth of the radius, being 0·43 to 0·7 mm. wide. The zoœcia bend from the axial to the mature zone at an angle of 25° to 45°, and the tubes meet the surface obliquely. The zoœcia are very thin-walled in the axial zone ; the walls in the mature zone are moniliform—there are usually two distinct rows of thickening, but these occasionally appear confluent ; at intervals of about 4 mm. or more arcuate axial rows of thickening are gradually given off from these peripheral rows. The length of individual monilæ in the mature zone is 0·22 to 0·38 mm.—the two rows are of sub-equal length—and their width up to 0·2 mm., though they are more often about 0·1 mm. in width. Each arcuate row of thickening is composed of a single row of smaller monilæ about 0·2 mm. long and 0·05 mm. wide. Thin complete diaphragms occur extremely infrequently in the axial region (the " tabulum " in a slide of this form figured by Etheridge (1892, pl. VII, fig. 9) is one of the monilæ cut obliquely). Small acanthopores originate close to the surface in the mature zone, up to about twelve surrounding each aperture.

Remarks : A section of a specimen of this form was figured by Etheridge (1892, pl. VII, fig. 9) as *Stenopora tasmaniensis* Lonsdale, which is a larger form, the diameter of the branches being, according to Lonsdale's original description, about twice the diameter of the branches of this species ; differences are shown also in the arrangement of the acanthopores and in the monilæ of the mature zone. No species which could be identified with *Stenopora tasmaniensis* appears to occur in New South Wales.

Stenopora frondescens sp. nov.

Plate XV, fig. 10 ; Text-fig. 4A, B.

Holotype : 3401. *Occurrence :* Westley Park Tuffs, Crinoidal Stage, Upper Marine Series, at Black Head, near Gerringong.

Frondescent Stenopora, *with a very narrow mature zone with two or three rows of monilæ, and a broad axial zone crossed by arcuate rows of monilæ ; acanthopores abundant ; mesopores numerous ; diaphragms extremely rare.*

The zoarium is composed of anastomosing frondescent branches which may cover an area of more than 30 cm. ; individual branches are from 9 to 14 mm. in thickness. On the surface of these branches there are regularly placed monticules 2 to 3 mm. in diameter, raised about 1 mm. above the surface ; the distance between the centres of adjacent monticules is 5 to 7 mm. The zoœcia in the monticules are thicker-walled than those on other parts of the surface, and mesopores are more numerous than usual. The apertures are oval, the longer axes parallel to the direction of growth ; their length is 0·35 to 0·6 mm., and their width 0·32 to 0·46 mm. ; 7 to 8·5 apertures occur in 5 mm. parallel to, and about 14 at right angles to, the direction of growth ; smaller mesopores are frequently developed at the angles of the zoœcia. Over a part of the surface the apertures are closed by a thin complete calcareous plate. The interspaces between adjacent apertures are broad and fairly flat, with numerous acanthopores.

In the central portion of the branch the tubes are normally thin-walled, but well-marked arcuate rows of thickening, spaced about 9 to 13 mm. apart and each consisting of a single row of monilæ, 0·24 to 0·36 mm. in length, and about 0·08 mm. wide, cross this central part ; between each of these stronger rows of thickening one or two very poorly developed rows may occur. Complete diaphragms are very infrequently developed. The zoœcia curve gradually from the axial to the mature zone, which is about 0·4 mm. in width, and shows either two or three well-developed rows of thickening ; from this outer zone of

monilæ the strong arcuate rows of thickening which cross the axial zone are gradually given off. The zoœcia are thin-walled in the axial zone ; the thickness of the walls at the level of the monilæ in the mature zone is up to 0·22 mm. Round or oval untabulated mesopores from 0·05 to 0·2 mm. in diameter are rather frequently developed in the mature zone. There is no mesial lamina. Acanthopores are very well developed, and may project 0·1 mm. above the surface ; they occur in a single row in the walls between adjacent apertures, but are more crowded at the angles of the zoœcia, especially where mesopores are developed ; sixteen to twenty acanthopores surround each aperture ; they are generally large, but a few smaller ones occur.

Remarks : The form of the zoarium, narrow mature zone, and abundant acanthopores, distinguish this form from described species of *Stenopora* ; it differs from species of *Amphiporella* Girty in lacking maculæ and in having complete diaphragms, and from species of *Stenocladia* Girty in wall structure and in the absence of a mesial lamina.

Stenopora grantonensis sp. nov.

Plate XV, figs. 3, 6 ; Text-fig. 1A-C.

Holotype : 2446. *Occurrence :* Berriedale Limestone, Granton Stage, at Granton Quarry, near Hobart, Tasmania.

Very fine, ramose Stenopora, *with a broad mature zone generally without well-marked monilœ, and a relatively narrow axial zone crossed by arcuate zones of thickening ; mesopores rare ; acanthopores very numerous.*

The zoarium is ramose, with cylindrical branches 1·6 to 2 mm. in diameter, which bifurcate at intervals of 7 mm. or more ; the angle between the branches after bifurcation is 65° to 85°. Neither monticules nor maculæ are developed. The zoœcia are not very regularly arranged, though they may form rough longitudinal or diagonal rows ; from about 9 to 10 apertures occur longitudinally in 10 mm. The apertures are elliptical, 0·35 to 0·4 mm. long and 0·17 to 0·22 mm. wide ; the interspaces between adjacent apertures are broad and slightly rounded, with generally two or more rows of fine acanthopores. Small, sub-circular mesopores, up to 0·17 mm. long, are rather infrequently developed. The mature zone is 0·33 to 0·5 mm. in radius ; the bend from the axial to the mature zone is gradual, at an angle of about 45° ; the thickness of the zoœcial walls in the mature zone is up to 0·22 mm., and is typically greater between consecutive than between laterally adjacent apertures. Generally the tubes are angular and very thin-walled in the axial zone, and oval with evenly thickened to slightly moniliform walls in the mature zone, but arcuate thickened zones cross the axial zone at relatively distant intervals ; they are developed usually within 3 mm. before bifurcation of a branch, and at intervals throughout the length of the zoarium ; each is less than 0·2 mm. in length, and typically they are composed of a single row of monilæ, though a second row may occur. Very rarely thin, complete diaphragms are developed in the zoœcia in the axial zone ; the mesopores are untabulated. Acanthopores are small and very numerous ; about 18 surround each aperture ; they are of two sizes, of which the smaller are more numerous ; the small acanthopores originate much closer to the surface than the larger ones. About ten apertures occur around the circumference of a transverse section.

Genus **Fenestrellina** d'Orbigny, 1849 (**Fenestella** Lonsdale, 1839).

Fenestrellina dispersa sp. nov.

Plate XV, figs. 4, 5.

Holotype : 3404. *Occurrences :* Ulladulla Mudstones, Upper Marine Series, at Warden Head, Ulladulla (holotype) ; Allandale Stage, Lower Marine Series,

at Jackson's Hill, Por. 132, Par. Pokolbin, and railway cutting east of Allandale Station ; Fenestella Shales, Branxton Stage, Upper Marine Series, at Branxton railway cutting, Por. 126, Par. Mulbring, Por. 15, Par. Belford, and Kitchener's Hill, near Cessnock ; Branxton Stage (above Fenestella Shales), in Wattle Ponds Creek, Por. 41, Par. Darlington ; Muree Stage, Upper Marine Series, at Abbey Green, Por. 44, Par. Wittingham ; Permian at Marlborough ; 1,000 feet above sea level, Huon Rd., Mt. Wellington ; Grange Quarry, near Hobart, Tasmania ; and Consuelo Creek (two miles above Cattle Creek) (Reid, 1930, 157, loc. 6), Springsure District, Queensland.

Fine Fenestrellina *with three zoœcia to a fenestrule and with a slight carina and small, regularly-spaced nodes ; colony infundibuliform with the celluliferous surface external.*

The colony is infundibuliform with the celluliferous surface external ; there are 17 to 23 branches horizontally, and generally between 12 and 16 fenestrules vertically, in 10 mm. The branches are straight, bifurcating at very distant intervals ; increase to three rows of zoœcia occurs immediately before bifurcation ; they show a slight median carina, on which there is a single row of small nodes placed from 0·24 to 0·4 mm. apart. The apertures are circular, about 0·12 mm. in diameter ; the distance between the centres of successive apertures is 0·24 to 0·33 mm. ; about 34·5 apertures occur in 10 mm., and three in the length of each fenestrule ; very thin peristomes surround the apertures, which do not project into the fenestrules. The fenestrules are sub-rectangular in shape, 0·46 to 0·71 mm. long and 0·13 to 0·33 mm. wide ; the dissepiments are rounded on both surfaces and are 0·13 to 0·24 mm. wide. The branches are 0·24 to 0·33 mm. wide ; they are thicker than the dissepiments, and are rounded on the reverse surface, which is finely granular and is ornamented by small to fairly large tubercles.

Remarks : This form is possibly the most widespread and abundant species of *Fenestrellina* in the Permian of eastern Australia ; it is a smaller species than *Fenestrellina fossula* (Lonsdale), with which it is commonly associated, and differs in the characters of the reverse surface. *F. texana* (Girty), 1908, from the Delaware Mountain formation, Southern Delaware Mountains, Texas, is a larger species, and has a very high carina with more closely and regularly spaced nodes.

The following species are recorded from additional localities :

Fenestrellina fossula (Lonsdale), 1844 : Dilly (Reid's Locality, 1930, 157) and Consuelo Creek (two miles above Cattle Creek) (Reid, 1930, 157, Loc. 6), Springsure District, Queensland.

Fenestrellina horologia (Bretnall), 1926 : Consuelo Creek (two miles above Cattle Creek) (Reid, 1930, 157, Loc. 6), Springsure District.

Fenestrellina granulifera Crockford, 1941*b* : Huon Rd., Mt. Wellington, Tasmania, 1,000 feet above sea level.[1]

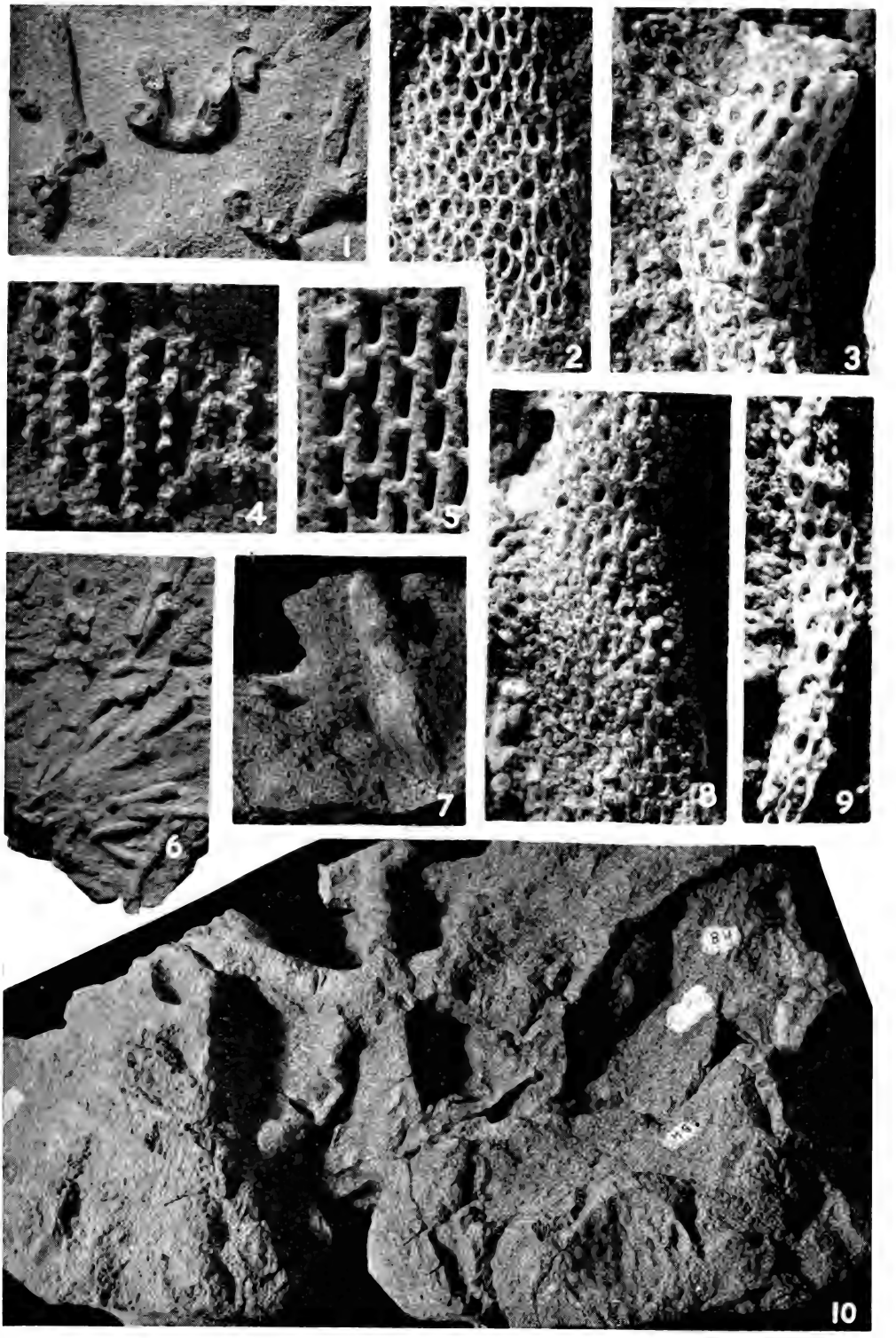
Fenestrellina altacarinata Crockford, 1941*b* : Fenestella Shales, Par. Coongevoi, just south of Por. 26, Par. Aellalong.

Polypora montuosa (Laseron), 1918 : Fenestella Shales, Kitchener's Hill, near Cessnock (Por. 50, Par. Quarrybylong).

Polypora virga Laseron, 1918 : Fenestella Shales, Par. Coongevoi, just south of Por. 26, Par. Aellalong.

Protoretepora ampla (Lonsdale), 1844 (s. str.) : A specimen from the Upper Marine Series in conglomerate on west side of Mudgee railway cutting,

[1] In the original description of this species, the distance between the nodes was given as " 0·37 mm." ; this should have been corrected to " 0·5 to 0·65 mm."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1¼ miles north of Rylstone (F.39640, Australian Museum Collection) is conspecific with specimens from Bundanoon tentatively referred to *Protoretepora ampla* (Lonsdale) (Crockford, 1941*a*, 406, pl. XIX, fig. 4).

Bibliography.

Bassler, R. S., 1929. The Permian Bryozoa of Timor. Paläontologie von Timor, XVI Lief., XXVIII Teil, 37. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

Bassler, R. S., 1941. Generic Descriptions of Upper Paleozoic Bryozoa. *Jour. Washington Acad. Sci.*, **31**, (5), 173.

Bretnall, R. W., 1926. Palæontological Contributions to the Geology of Western Australia, VII, (XIII). Descriptions of some Western Australian Fossil Polyzoa. *Bull. geol. Surv. W.A.*, 88.

Crockford, Joan, 1941*a*. Permian Bryozoa of Eastern Australia. Part I. A Revision of Some Previously-named Species of Fenestrellinidæ (Fenestellidæ). *Jour. Roy. Soc. N.S.W.*, **74** (for 1940), (IV), 397.

Crockford, Joan, 1941*b*. *Ibid.* Part II. New Species from the Upper Marine Series of New South Wales. *Jour. Roy. Soc. N.S.W.*, **74** (for 1940), (IV), 502.

Dana, J. D., 1849. Fossils of New South Wales. *In* Wilkes' U.S. Exploring Expedition, X, Geology, Appendix and Atlas. Philadelphia.

Duncan, Helen, 1939. Trepostomatous Bryozoa from the Traverse Group of Michigan. *Michigan Univ. Mus. Pal., Contr.*, **5**, (10), 171.

Etheridge, R., Jnr., 1892. A Monograph of the Carboniferous and Permo-Carboniferous Invertebrata of New South Wales. Part I. Coelenterata. *Mem. geol. Surv. N.S.W., Pal.*, **5**, (2).

Girty, G. H., 1908. Guadalupian Fauna. *Prof. Paper U.S. geol. Surv.*, 58.

Girty, G. H., 1911. New Genera and Species from the Fayetteville Shale of Arkansas. *Ann. New York Acad. Sci.*, **20** (for 1910), 189.

Lee, G. W., 1912. The British Carboniferous Trepostomata. *Mem. geol. Surv. Great Britain, Pal.*, **1**, (3), 135.

Lonsdale, W., 1844. Description of Six Species of Corals, from the Palæozoic Formation of Van Diemen's Land. *In* Darwin, Geol. Obs. on Volc. Is., Appendix, 161. Smith, Elder and Co., London.

Lonsdale, W., 1845. Polyparia. *In* Strzelecki, Phys. Descr. N.S.W. and Van Diemen's Land, VI, Zoology, Palæozoic Fauna, 262. Longman, Brown, Green and Longmans, London.

Nicholson, H. A., and Etheridge, R., Jnr., 1886. On the Tasmanian and Australian Species of the Genus *Stenopora*. *Ann. Mag. Nat. Hist.*, Ser. V, **17**, 173.

Orbigny, A. d', 1849. Descriptions de Quelques Genres Nouveaux de Mollusques Bryozoaires. *Rev. Mag. Zool.*, 2e Ser., Tome I, 499.

Reid, J. H., 1930. Geology of the Springsure District. *Queensland Government Mining Jour.*, **31** (April), 149.

Ulrich, E. O., 1890. Palæozoic Bryozoa. *Geol. Surv. Illinois*, **8**, (2), sect. IV.

Explanation of Plate.

Figs. 1, 2.—*Stenopora gracilis* (Dana). 1. (Specimen 410), natural size. 2. Surface of branch (Specimen 3405). ×10.

Figs. 3, 6.—*Stenopora grantonensis* sp. nov. 3. Surface of holotype. ×10. 6. Natural size.

Figs. 4, 5.—*Fenestrellina dispersa* sp. nov. 4. Obverse surface of holotype. ×10. 5. Reverse surface of holotype. ×10.

Fig. 7.—*Stenopora nigris* sp. nov. Part of holotype. Natural size.

Fig. 8.—*Dyscritella porosa* sp. nov. Part of holotype. ×10.

Fig. 9.—*Dyscritella restis* sp. nov. Part of holotype. ×10.

Fig. 10.—*Stenopora frondescens* sp. nov. Part of holotype. ×½.

Photographs by H. G. Gooch.

THE ACTION OF SOLVENTS ON TORBANITE AND THE NATURE OF EXTRACTED PRODUCTS.

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Manuscript received, November 18, 1942. Read, December 2, 1942.

Summary.

The paper deals with the action of solvents on torbanite, the general principles of extraction and the nature of the extracted products. It is shown that, in general, aromatic compounds are more efficient solvents than those of aliphatic nature. Evidence bearing on the mechanism of solvent action is discussed, and the conclusion is drawn that thermal extraction depends on the preliminary absorption of the solvent by the organic matter at an early stage in the depolymerisation, followed by solution in the absorbed solvent at a later stage. Some important treatment principles are suggested, and the results of a preliminary examination of the products of benzene extraction are recorded.

Introduction.

Preliminary work on the extraction of oil from torbanite by solvents (Dulhunty, 1942) has shown that the organic matter normally insoluble in common organic solvents, may be rendered almost completely soluble by heating at temperatures considerably below those which cause thermal decomposition into gas, oil vapour and carbon. This change to the soluble form, occurring between 340° and 400° C., has been described as a form of depolymerisation (Dulhunty, 1942, and Cane, 1942). It precedes later thermal decomposition and evolution of oil vapours which take place above 400° C. when torbanite is heated comparatively rapidly, as in the usual retorting process. It has been shown also that the rate of depolymerisation and conversion to the soluble form are functions of both time and temperature. As much as 90% of the organic matter has been extracted in the form of oil by preheating and extraction with benzene under pressure.

Solvent Action.

Relative Solvent Properties of Some Different Organic Substances.

Results recorded previously by the author (Dulhunty, 1942) were based on benzene extraction of preheated torbanite. Subsequent work on the relative solvent properties of various compounds has shown that only some of the common organic solvents are suitable for complete extraction of the soluble products. The following qualitative experiments were carried out with the object of comparing the relative efficiency of different solvents for use in low temperature extraction of preheated torbanite, as well as extraction of unheated torbanite at the temperature necessary to render the organic matter soluble.

Experimental.

Preliminary tests were made to determine the ability of different solvents to redissolve the products extracted with benzene. It was found that chloroform, pyridine, quinoline, tetralin, carbon tetrachloride, coal tar naphtha, toluene and torbanite crude oil distillate (B.P. 150–230° C.), all readily dissolve the extracted products at room temperature, and solutions of

high concentration were built up without the precipitation of any of the solute. Naphthalene, which was tested at temperatures slightly above its melting point, completely dissolved the extract. Ethyl ether, ethyl alcohol and light petroleum (B.P. 40–60° C.) would dissolve only a portion of the extract, even in the case of hot solutions of low concentration. Petroleum kerosene dissolved the extract completely at temperatures above 200° C., but small quantities were precipitated on cooling, especially from concentrated solutions.

A series of experiments was carried out to test the ability of different solvents to extract the soluble products from preheated torbanite. Finely powdered torbanite, preheated at 380° C. for 4 hr., was extracted with each of the solvents mentioned in the above experiment, at their respective boiling points under atmospheric pressure, for a period of 24 hr. After cooling, the solid residues were separated from the extract solutions by filtration, and were washed with cold solvent until the washings were no darker in colour than the fresh solvent. They were then washed with fresh hot solvent—any further removal of material being indicated by the depth of colour of the washings—and were finally washed with cold benzene. In all cases black extract solutions were produced. The residues from the extractions with chloroform, carbon tetrachloride, tetralin, toluene, torbanite crude oil distillate, and coal tar naphtha, did not appreciably colour the washings from the hot fresh solvents and cold benzene. The residues from the pyridine and quinoline extractions, after being washed with cold solvent, coloured the washing from the hot solvents, but did not yield any further solute when washed with cold benzene. In the case of extractions with ethyl alcohol, ethyl ether, light petroleum and petroleum kerosene, the washings from the hot fresh solvents were slightly coloured and those from cold benzene considerably coloured.

A further series of experiments was carried out to determine the suitability of selected solvents for the extraction of torbanite at temperatures above 350° C. (these temperatures being necessary to render the organic matter soluble) with the object of eliminating preheating by dissolving the soluble products as they are formed. The pressure vessel used in this work has been described (Dulhunty, 1942). The critical temperature regions of the solvents were tested by heating them in the pressure vessel to a temperature of 410° C., and plotting the pressure-temperature relations. Those which gave curves showing sudden increases in pressure below, or approaching, 400° C., were discarded as they could not be kept in the liquid phase at the extraction temperature. The solvents were also examined for decomposition, or polymerisation, resulting from the high temperature. Those selected for high temperature extraction were coal tar naphtha (B.P. 150–220° C.), petroleum kerosene (B.P. 190–210° C.), and torbanite crude oil distillate (B.P. 230–260° C.). Tetralin and quinoline should be suitable, but sufficient quantities were not available for testing when these experiments were made.

The extractions were carried out by mixing 1 lb. of powdered torbanite with 1 lb. of solvent, and heating at a temperature of 390° C. for a period of 4 hr. After cooling the volume of residual gas was measured, and the extract solution separated from the solid residue by filtration. The residues were first washed with the fresh solvents, then with benzene and finally extracted with benzene under pressure at 200° C. The residues from the extractions with coal tar naphtha, and torbanite crude oil distillate, did not yield any further solute when washed with benzene and subjected to pressure-benzene extraction. The residue from the petroleum kerosene extraction yielded a considerable quantity of solute to the benzene washing, and a small quantity to the pressure-benzene extraction.

Conclusions.

The preliminary tests on the solubility of the benzene extract in different solvents show that aromatic compounds are more effective solvents than those of aliphatic nature. Ethyl alcohol, ethyl ether and light petroleum are entirely unsuitable as they dissolve only a portion of the extract. Petroleum kerosene is somewhat more efficient owing to the high temperature at which it may be used but some of the extract is precipitated on cooling. Torbanite crude oil distillate possesses good solvent properties which are probably due to the presence of considerable quantities of cyclic compounds.

V—December 2, 1942.

The extractions of preheated torbanite at atmospheric pressure, and at the boiling points of the different solvents, indicate that ethyl alcohol, ethyl ether, light petroleum and petroleum kerosene are capable of dissolving only a portion of the soluble product, and they precipitate some of their solute on cooling. Pyridine and quinoline appear to extract all the soluble product, but precipitate some constituents on cooling. The aromatic solvents and torbanite crude oil distillate, completely extract the soluble products, and are capable of holding all the extracted material in solution when cold. The low boiling aromatic solvents can be separated from the extracted products by fractional distillation, but those of high boiling point (150° C. and over) cannot be recovered successfully in this way.

The results of the pressure extractions at 390° C., using torbanite which had not been preheated, indicate that coal tar naphtha and torbanite crude oil distillate are capable of complete extraction, and of holding all the extract in solution when cold. Petroleum kerosene is somewhat less efficient in its solvent properties, leaving a small residue of unextracted product as well as precipitating a considerable quantity of its solute when cold. Coal tar naphtha, which underwent some decomposition and polymerisation at the high temperature of the extraction, is an efficient solvent, but cannot be separated from the extracted products by distillation. Petroleum kerosene and torbanite crude oil distillate both underwent a considerable amount of cracking with the production of gas, spirit and carbon. In the case of torbanite crude oil distillate, however, the heavy portion of the solvent oil was replaced by oils extracted from the torbanite, giving a final oil stock similar in volume and composition to the original solvent oil. This result suggests the possibility of eliminating the preheating process by using torbanite oil as the solvent at temperatures between 350° and 400° C., in such a way that the cracking of the oil, which inevitably occurs in the presence of torbanite at these temperatures, could be controlled to give an efficient production of spirit; the solvent oil stock being simultaneously replaced by oils extracted from the torbanite. Further work along these lines is being carried out at present.

Mechanism of Solvent Action.

Experimental work on solvent extraction of torbanite has produced evidence which suggests that the physical action of solvents is not a simple surface solution effect. This evidence is as follows:

(i) Tests were carried out to determine the effect of the particle size of torbanite powder on solvent extraction. Unexpected results were obtained: torbanite powdered to a maximum particle size of 0·2 mm., and the same material in a granular condition in which the fragments averaged 5 mm. in diameter, yielded exactly the same quantity of solute and required the same length of time for complete extraction. A one-inch cube of torbanite was preheated at 375° C. for 1 hr., which produced a "rubbery" condition; but the block was tough and could not be broken by hand. It was then heated in torbanite crude oil at 200° C. for 1 hr., after which it appeared swollen and could be crushed readily in the hand. When granular torbanite, which has been preheated so as to render a portion of the organic matter soluble, is extracted with a solvent such as benzene or torbanite oil, the particles swell considerably, in some cases to almost twice their original size.

(ii) When unheated torbanite, either powdered or granular, is mixed with torbanite oil and heated at a temperature below 250° C. (too low to cause depolymerisation of the organic matter) there is no difficulty in subsequently filtering the solid material from the oil. If it is heated with the oil at a temperature above 300° C., which is sufficient to cause depolymerisation and conversion to the soluble form, for a length of time to render only a portion of the organic

matter soluble, it is impossible to separate the oil from the solid material by filtration, even using strong suction. If, however, the heating is continued until complete, or almost complete, conversion to the soluble state is effected, the extremely fine-grained, solid residue can be separated by filtration with ease and rapidity.

(iii) It has been shown by pressure-benzene extraction (Dulhunty, 1942) that less than 1% of the organic matter can be extracted from torbanite by heating it with a solvent at 270° C. for 8 hr. Later work has shown, however, that this treatment causes swelling and softening of the powder, and it is difficult to separate it from the solvent by filtration after heating.

The foregoing evidence is interpreted as follows : Torbanite undergoes no change at all when heated at temperatures below 250° C. ; between 250° and 300° C. depolymerisation of the organic matter commences, and some solvent is absorbed by the torbanite particles, which become soft and swollen, although no appreciable quantity of soluble product is formed ; with continued heating between 300° and 350° C., depolymerisation continues and a considerable quantity of soluble product is formed, and more solvent is absorbed with further swelling and softening of the particles, accompanied by a partial breakdown in the physical structure of the torbanite which forms an intimate mixture with the solvent and produces a jelly-like mass which cannot be filtered. Continued heating between 350° and 400° C. causes the organic matter to dissolve in the solvent it has absorbed, producing a complete breakdown in the physical structure of the torbanite and the formation of a true solution of the organic matter in the solvent oil, accompanied by the separation of free carbon and inorganic matter which can be removed readily by filtration.

Conclusions Concerning Treatment Principles.

Some important conclusions concerning treatment principles can be drawn from the foregoing results and discussion.

(*a*) It is evident that the production of oil from torbanite by solvent extraction may be accomplished in at least two different ways : (i) by preheating the torbanite at temperatures between 350° and 400° C. for a sufficient length of time to render the organic matter soluble, and then extracting the soluble products with a suitable low-boiling solvent such as benzene, followed by the separation of the solvent from the solute by distillation. In this method the product of extraction is the depolymerised organic matter which has not undergone cracking into light oils and spirit. It is a heavy oil which would require further treatment, such as cracking or hydrogenation, for the production of light fuel oil or motor spirit. (ii) By extracting the torbanite with its own oily extract at temperatures between 350° and 400° C. and under pressures between 150 and 300 lb./sq. in. In this method the preheating and extraction occur simultaneously, and at the same time the solvent oil stock is cracked, with the production of gas and carbon, into lighter oils and spirit, and is replaced by the extracted oils. The products of the extraction are gas, spirit, carbon and solvent oil, which is a mixture of hydrocarbons at all stages of cracking from the depolymerised organic matter to light oils. The cracking which occurs during the extraction can be controlled to give optimum yields of motor spirit, or light fuel oil, as required. In both the above methods, the yields of final products are much higher than those obtained by first retorting torbanite and then cracking the crude oil, as the inefficient cracking associated with the retorting process is substantially eliminated.

(*b*) The absorption of the solvent by partially depolymerised torbanite, and the difficulty in separating such material from an extract solution, mean that residues containing unextracted oils, due to insufficient preheating in (*a*) (i) above, cannot be returned for further preheating and extraction unless

a method of washing and decantation is adopted, such as that used by the author (Dulhunty, 1942) in experimental work.

(*c*) Success in separating the solid residues from the extract solution, by any type of filtration, depends on the complete extraction of the torbanite.

(*d*) The fact that solvent extraction depends on the preliminary absorption of the solvent, rather than a simple surface solution effect, means that it is not necessary to reduce the torbanite to a fine powder for solvent extraction.

(*e*) The solution of the organic matter is accomplished by the solvent which the torbanite absorbs, thus comparatively small quantities of solvent are required, good results being obtained by using quantities varying from 1 : 1 to 2 : 1 by weight of solvent and torbanite respectively. It also follows that stirring is not essential.

(*f*) The difficulties involved in preheating dry, powdered or granular torbanite, evenly throughout its bulk, make it desirable to adopt a method in which preheating and extraction are effected simultaneously in the presence of a solvent oil.

Preliminary Examination of Extracted Products.

The material examined was the product obtained by preheating torbanite at temperatures between 360° and 380° C. for periods varying from 2 to 6 hr., followed by pressure-benzene extraction at 260° C., and the separation of the solute from the benezene by fractionation. (See (*a*) (*i*) under Treatment Principles.) Particular care was taken to ensure that the final product was free from benzene.

(*a*) *Physical Properties.* Just fluid at room temperatures ; flowing freely above 40° C.

Colour : Black ; completely opaque.

Odour : Faint aromatic odour, quite distinct from that of crude oil produced by retorting torbanite, and faintly resembling the odour of heavy residues from the distillation of coal tar.

Specific gravity : 0·92 at 20° C.

Refractive index : 1·55 at 20° C.

(*b*) *Distillation at Atmospheric Pressure.* A small quantity of distillate was obtained amounting to about 16% by volume of the original product, and boiling from 150° to 275° C. Distillate below 275° C. was pale yellow to light red in colour, comparatively colour-stable, and possessed the odour of the original product. Cracking commenced when the vapour temperature reached 275° C., and the distillate obtained was light red in colour but darkened to dark red soon after distillation and eventually became black. This distillate contained a " light end ", and possessed the odour of retort crude oil.

(*c*) *Distillation under Reduced Pressure.* Distillate amounting to 30% by volume of the original product was obtained, boiling from 60° to 250° C. under 15 mm. of mercury. Cracking commenced when the vapour temperature reached 250° C. Distillate from 60° to 170° C. was pale yellow to light red, and colour-stable, and paraffin wax separated on standing, but the oils did not possess the properties of lubricants. Residue above 250° C. was solid at room temperatures, but soft and greasy, melting at 60° to 80° C.

(*d*) *Fractional Solution.* The product was extracted with light petroleum (B.P. 40°-60° C.) at 50° C. The soluble fraction was separated from the light petroleum and distilled under reduced pressure. The fraction insoluble in light petroleum, was extracted with ethyl alcohol at 60° C. The fraction

insoluble in alcohol, was boiled with 20% sodium hydroxide for 3 hr., filtered, and the filtrate acidified with hydrochloric acid. The results were as follows:

(i) Fraction soluble in light petroleum: 87% by weight, 88·5% by volume, black oil, fluid at room temperatures, specific gravity 0·914, refractive index 1·5211, odour of original product, distillation under reduced pressure, see Table I.

(ii) Fraction insoluble in light petroleum: 13% by weight, 11·5% by volume, black solid, brittle at room temperatures, softening point about 100° C., odourless, refractive index 1·6452, specific gravity 1·04.

(iii) Fraction insoluble in light petroleum but soluble in ethyl alcohol: about 2·5% by weight, black semi-solid, tarry material.

(iv) Fraction insoluble in light petroleum and ethyl alcohol: Black solid, brittle at room temperatures, softening point about 100° C., odourless, refractive index 1·6498, specific gravity 1·05. The treatment with sodium hydroxide had no effect, the alkaline solution was not coloured, and the filtrate gave no precipitate when acidified.

Conclusions.

The results of distillation under atmospheric and reduced pressures suggest that the product consists largely of very heavy paraffin compounds, including waxes and, possibly, substances of even higher molecular weight from which the waxes were derived. The lighter fractions obtained by distillation under reduced pressure possess a pale yellow colour, which does not become darker on standing. This would suggest the absence of those compounds which cause the rapid darkening in colour of all distillates from retort crude oil. The light-petroleum-insoluble fraction evidently represents the source from which the soluble oils were derived, as further heat treatment renders it soluble. Work being carried out shows that there is no accumulation of residue, insoluble in light petroleum, when successive extractions of torbanite are made with previously extracted oils at temperatures between 350° and 400° C. From this it would seem that the difference between the fractions, soluble and insoluble in light petroleum, depends on the degree of depolymerisation rather than any fundamental difference in chemical nature. Only 2·5% of the light-petroleum-soluble fraction is soluble in ethyl alcohol, indicating the absence of soluble resinous material in any appreciable quantity. The fact that this fraction is not attacked by hot alkali seems to suggest the absence of soluble ulmins and tar acids.

Table I.

Vacuum Distillation of Light-petroleum-soluble Fraction of Product from Pressure-benzene Extraction of Preheated Torbanite.

(Pressure of distillation, 18 mm. of mercury.)

Boiling Range: Reduced Pressure. ° C.	Calculated Boiling Range: Atm. Pressure. ° C.	Per Cent. by Volume of Original Product.	Specific Gravity.	Refractive Index.
85–120	150–210	8·67	0·7909	1·45
120–140	210–245	3·55	0·8347	1·46
140–180	245–290	5·92	0·8478	1·47
180–220	290–335	6·70	0·8672	1·48
220–250	335–370	6·31	0·8865	1·49
Residue	—	60·95	0·9721	1·54
Original product ..	—	—	0·9264	1·53
Light - petroleum - soluble fraction ..	—	88·5	0·9148	1·52
Light - petroleum - insoluble fraction	—	11·5	1·04	1·64

The results of the distillation of the light-petroleum-soluble fraction under reduced pressure are summarised in Table I. The very heavy nature of the oil is emphasised by the fact that only 39%, by volume, boils below a temperature equivalent to about 370° C. at atmospheric pressure. The specific gravities and refractive indices of the various fractions increase with the boiling ranges, and the values found for the residue from the distillation, are considerably higher than those of the heaviest fraction distilled, indicating the presence of very heavy hydrocarbons, possessing high refractive indices and specific gravities.

Acknowledgments.

In conclusion the author wishes to acknowledge valuable discussion with Messrs. L. J. Rogers and E. J. Kenny, and members of the staff of National Oil Pty. Ltd. and the departments of Chemistry and Engineering Technology of the University of Sydney. Valuable technical assistance was also given by Messrs. A. J. Tow and I. S. Haviland, University of Sydney, in connection with the examination of extracted products and other chemical work.

References.

Cane, R. F., 1942. *Proc. Roy. Soc. N.S.W.*, **76**, 190.
Dulhunty, J. A., 1942. *Proc. Linn. Soc. N.S.W.*, **67**, 239.

THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

Part VI. Pyridine Complexes of Rhodous Halides.

By F. P. Dwyer, M.Sc.,
and R. S. Nyholm, M.Sc.

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In previous communications (Dwyer and Nyholm, 1941, 1942), a number of arsine coordinated rhodous halides, prepared by the reduction of the corresponding rhodic compounds with hypophosphorous acid, were described. This method has now been applied to the preparation of a number of pyridine coordinated complexes. Reduction in the presence of excess of pyridine gave the hexakis compounds, which by subsequent treatment with acids yielded other derivatives, but all with the common coordination number of six. By reason of the ease of oxidation of the iodides, and unsuitable solubility relationships in the chloride series, it has been possible to work out the whole series, with one exception, with the bromides only. However, there is little doubt that under suitable experimental conditions the various reactions involved are general for the whole halogen group.

The hexakis pyridine bromo compound (II) was easily formed by the reduction of the rhodic compound (I) formed *in situ*, by hypophosphorous acid at 100° C., and obtained in pale yellow crystals by cooling in carbon dioxide to 0° C. Treatment with ice cold hydrobromic acid gave the pale yellow crystalline pentakis compound (III). One halogen atom in this compound was ionised in aqueous solution, and treatment with potassium iodide at room temperature gave the bromo-iodide (IV), which could be reconverted to the bromide (III) by treatment with excess of potassium bromide. By heating in aqueous solution with potassium iodide, the second bromine atom in (IV) could be replaced to yield iodo-pentapyridine rhodous iodide.

The pentakis compound (III) when refluxed with hydrobromic acid in the presence of a trace of hypophosphorous acid gave the highly insoluble pale buff tetrakis compound (V) which was stable towards boiling aqueous hydrobromic acid, but transformed into the darker tris-pyridine dimeride (VI) by treatment with alcoholic hydrobromic acid. Compound (VI) is the pyridine analogue of the tris-arsine complexes previously described. Long boiling with alcoholic hydrobromic acid gradually dissolved (VI) yielding a red solution from which a small amount of red-brown crystals of the two pyridinium salts (VII) and (VIII) was deposited, leaving a reddish solution containing (probably) the very soluble pyridinium salt (IX). An excellent yield of a mixture of the two pyridinium salts (VII), (VIII) was obtained by treatment of any of the previous compounds with alcoholic hydrobromic acid containing pyridinium bromide. By prolonged boiling, the Compound (VII) in the mixture was gradually transformed into (VIII). Although the pyridinium salt (VII) was not obtained pure in the bromide series, pure specimens of both (VII) and (VIII) were obtained in the chloride series.

The easily water-soluble compound (IX) which was not isolated owing to its high solubility is put forward as the logical end of the series, since it is inconceivable that the halogen bridged dimeric structures which have been maintained

so consistently from compound (VI) onwards should suddenly revert to the normal monomeric octahedral type. It is significant that the transformation from the monomeric tetrakis compound (V) to the bridged type of structure still occurs when (V) is treated with pyridinium hydrobromide and hydrobromic acid, when the monomeric structure might well be maintained by the formation of compounds such as $PyH(RhBr_3 . 3Py)$. It is proposed to attempt the preparation of compounds of type (IX) shortly.

In the chloride series the reaction could not be stopped at stages corresponding to compounds (V), or (VI), presumably owing to higher solubilities than with the corresponding bromides, and even the chloro compound of type (IV) was difficult to obtain pure.

The iodide series gave the only analytically pure specimen of the hexakis compound of type (I), which could be washed free of impurity with aqueous pyridine by reason of its relatively low solubility. The compound lost one molecule of pyridine if it was washed with water, and was highly sensitive to oxidation—as might be expected from its two ionisable iodine atoms. Similarly the preparation of the pentakis iodo compound of type (II) was easily achieved, but all attempts at the preparation of other compounds failed owing to self oxidation and the liberation of hydrogen from hot acid solutions. In the presence of hypophosphorous acid designed to prevent this oxidation, the evolution of hydrogen became even more violent, and the same purplish-brown compound was obtained. In a series of experiments using the bromo-iodo compound (IV), which in the presence of potassium iodide in hot solution is transformed into di-iodo compound, it was found that the characteristic darkening and the deposition of the purplish brown compound did not occur until hypophosphorous acid was added. This suggested that the reaction involved the reduction to monovalent rhodium—possibly $RhPy_5I$—and this compound was then instantly decomposed with the evolution of hydrogen. It is curious that this reaction occurs only with the iodide, and this suggests that the intermediate of a monovalent compound is feasible since the reduction potential is generally lowest with the iodide. The compounds obtained were usually variable in composition, but two compounds gave analyses consistent with a formula $Rh_2Py_5I_5$, which is possibly a compound of bivalent and trivalent rhodium.

All of the compound prepared reduced alcoholic silver nitrate to the metal, but curiously enough the reduction was slow and very incomplete in aqueous solution. The colour of the compounds darkened progressively as the coordinated pyridine was removed—thus the hexakis compounds were yellow, and the pyridinium salts were red or reddish brown.

Experimental.

Hexakis-pyridine rhodous bromide (*II*). Rhodium trichloride solution (20 mls.), containing 0·176 g. of rhodium, was treated with potassium bromide (10 g.) and pyridine (10 mls.). The mixture was heated to boiling to form the coordinated rhodic compound, and then treated whilst hot with hypophosphorous acid (3 mls. of 30%) solution. It was boiled for a further one minute, when the colour diminished somewhat, and then rapidly cooled in ice to 0° C. in the presence of carbon dioxide, when glistening yellow rhombs of the required compound came down. It was difficult to purify owing to its solubility in water, and even after washing with aqueous pyridine gave unsatisfactory analyses due to the presence of potassium bromide. This substance could be detected by dissolving in alcohol in which the impurities were insoluble. The compound in aqueous solution instantly precipitated the whole of its bromine, and further evidence of its ionisation was given by its precipitation due to the common ion effect by the addition of bromides. The alcoholic solution of the compound reduced hot alcoholic silver nitrate to the metal.

Bromo-pentakis-pyridine rhodous bromide (*III*). The hexakis compound prepared as before was cooled in ice and treated with constant boiling hydrobromic acid (15 mls.), when golden yellow flat plates of the pentakis compound were precipitated. The precipitate was washed with ice

cold 1 N. hydrobromic acid in which it is nearly insoluble, and then rapidly with ice water in which it is easily soluble. An aqueous alcoholic solution instantly precipitated part of the bromine in the cold, and the remainder on heating, followed by reduction of the silver nitrate to the metal. The compound was easily soluble in alcohol and acetone, but insoluble in benzene. In the air it darkened due to oxidation, but the rhodic compound formed was easily removed by washing with water containing a trace of hydrobromic acid. In the preparation of this compound and of the previous one, if the boiling with hypophosphorous acid is prolonged, small yields only are obtained, and some metallic rhodium is produced. This suggests that the reduction possibly proceeds to the monovalent stage, and this view is supported by the evolution of hydrogen when such highly reduced solutions are acidified.

Found: Rh, 15·6%; Br, 24·2%. Calculated for $(Rh(C_5H_5N)_5Br)Br$: Rh, 15·63%; Br, 24·31%.

Bromo-pentakis-pyridine rhodous iodide (*IV*). Bromo-pentakis-pyridine rhodous bromide (0·5 g.) was dissolved in warm water, which had been previously freed from dissolved air and saturated with carbon dioxide. The clear yellow aqueous solution was filtered from traces of impurity, a few drops of hypophosphorous acid added, heated to 80° C. for a few minutes and then cooled to room temperature. Potassium iodide (1 g.) was then added and gave a voluminous pale yellow precipitate of the required compound. The precipitate was washed once with water, then several times with very dilute hydriodic acid, and finally once with ice water in which it is quite soluble. It was dried over concentrated sulphuric acid. The compound was precipitated from its aqueous solution by the addition of potassium iodide. In the cold alcoholic silver nitrate precipitated immediately all of the iodine as silver iodide, and on heating the bromine as silver bromide, and finally was reduced to metallic silver.

Found: Rh, 14·9%; calculated for $(Rh(C_5H_5N)_5Br)I$: Rh, 14·62%.

Dibromo-tetrakis-pyridine rhodium (*V*). Bromo-pentakis-pyridine rhodous bromide (0·4 g.) was refluxed with 2 N. hydrobromic acid (30 mls.) in the presence of a few drops of hypophosphorous acid. The substance was gradually dissolved to a yellow solution, and then replaced by a voluminous pale buff precipitate. The refluxing was continued for a further five to ten minutes to increase the particle size, and after filtering was washed many times with warm water. It was insoluble in water and benzene, but slightly soluble in alcohol or acetone. The alcoholic solution gave no reaction with cold alcoholic silver nitrate, but precipitated a mixture of silver bromide and metallic silver on boiling. The substance, which crystallised in minute needles, was stable in air, and not affected by long boiling with aqueous hydrobromic acid.

Found: Rh, 17·8%; Br, 27·35%. Calculated for $(Rh(C_5H_5N)_4Br_2)$: Rh, 17·78%; Br, 27·64%.

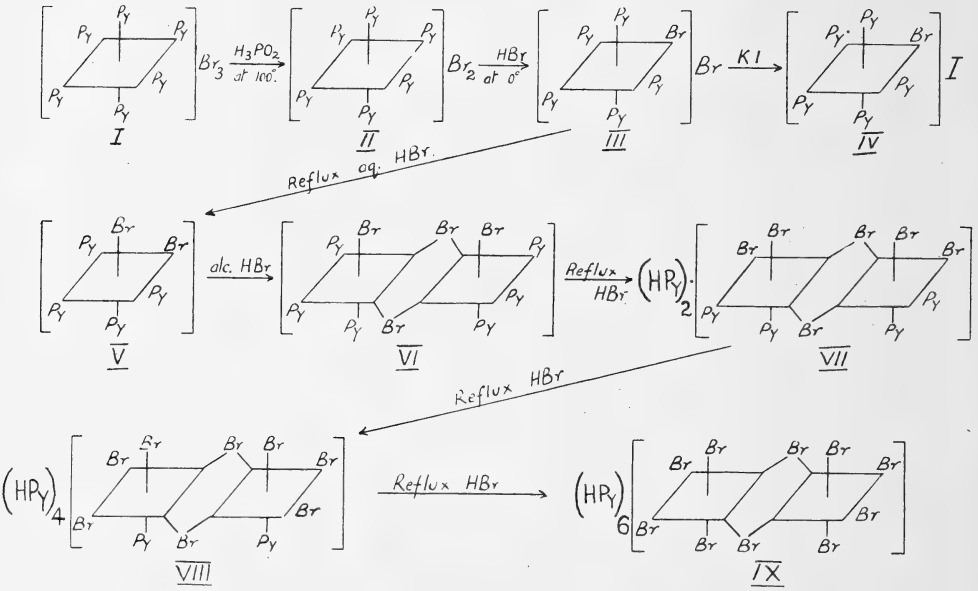
Dibromo-hexakis-pyridine μ *dibromodirhodium* (*VI*). Finely powdered dibromo-tetrakis-pyridine rhodium (0·8 g.) was refluxed with constant boiling hydrobromic acid (12 mls.), water (12 mls.), alcohol (20 mls.) and 30% hypophosphorous acid (7 drops). The substance gradually darkened in colour, commencing to dissolve after about five minutes. After approximately 50% had dissolved, the substance was filtered whilst hot, and the reddish filtrate reserved. The precipitate was well washed with hot 50% alcohol, and dried over sulphuric acid. The substance was insoluble in water, and sparingly soluble in hot alcohol, acetone, or chloroform. The substance was also more stable to heat than any of the compounds previously described.

Found: Rh, 20·2%; Br, 31·5%. Calculated for $(Rh(C_5H_5N)_3Br_2)_2$: Rh, 20·18%; Br, 31·37%.

Bis-pyridinium-tetrabromo-tetrakis-pyridine μ *dibromodirhodium* (*VII*) *and Tetrakis-pyridinium-hexabromo-bis-pyridine dibromodirhodium* (*VIII*). The bright red filtrate from the preparation above on cooling deposited reddish buff twinned needles and plates. After filtering from the still reddish mother liquor, and well washed with water, it was dried over sulphuric acid. The filtrate from which no further crystalline material could be obtained, is considered to contain the last substance in the degradation series, since the crystalline material by refluxing with alcoholic hydrobromic acid can be transformed into the same reddish water-soluble compound, which is considered to be hexakis-pyridinium-octabromo dibromodirhodium (IX).

The crystalline material gave the following analyses for different preparations: Rh, 15·62%, 16·02%, 15·83%, 15·70%, 16·1%; Br, 44·06%, 41·0%, 41·6%, 41·56%, 39·36%. Calculated for $(C_5H_5N.H)_2(Rh_2Br_6(C_5H_5N)_4)$: Rh, 17·68%; Br, 41·4%. Calculated for $(C_5H_5N.H)_4(Rh_2Br_8(C_5H_5N)_2)$: Rh, 15·56%; Br, 48·34%.

Attempts to separate the mixtures by extraction with solvents were fruitless owing to their sparing solubility; but ultimately the tetrakis pyridinium compound was isolated by prolonged treatment with boiling hydrobromic acid in aqueous alcoholic solution. The best yields of the pyridinium salts were obtained by the following procedure: tetrakis pyridine dibromo rhodium (V) (0·8 g.) was refluxed with constant boiling hydrobromic acid (14 mls.), water (14 mls.), hypophosphorous acid (5 drops) and a mixture of pyridine (6 mls.) and hydrobromic acid (12 mls.). The boiling was continued until the tris pyridine compound which is the first decomposition product had just dissolved. The heavy beautifully crystalline red pyridinium salts were well washed with water, and dried at 100° C. By further action with squeous alcoholic hydrobromic



acid, the bis pyridinium salt was gradually transformed into the tetrakis compound, which also decomposed slowly to the compound (IX), which contains no coordinated pyridine.

Found for purified product: Rh, 15·6%, 15·62%; Br, 49·77%, 47·4%.

The pyridinium salts were somewhat soluble in alcohol in the absence of pyridinium bromide or bromides. They were soluble in aqueous sodium hydroxide to orange solutions, which had a powerful odour of pyridine and were reprecipitated by acids. With silver nitrate they gave a voluminous precipitate of silver bromide and metallic silver on heating.

Hexakis-pyridine rhodous chloride. This was prepared in a manner similar to the bromide, save that potassium chloride was substituted for the potassium bromide. On cooling in ice and salt glistening pale yellow crystals of the compound came down, together with some potassium chloride. The substance was exceedingly soluble in water except in the presence of metallic chlorides, and thus a sample suitable for analysis could not be obtained. The substance darkened in the air owing to oxidation, instantly precipitated all of its chlorine by the addition of alcoholic silver nitrate which was reduced to the metal on heating. The substance was very soluble in alcohol and acetone.

Chloro-pentakis-pyridine rhodous chloride. The hexakis compound prepared as above was cooled in ice and treated with ice cold 5 N. hydrochloric acid (30 mls.), when very pale yellow

flat plates were precipitated. The precipitate was washed with ice cold dilute hydrochloric acid, and finally with a small amount of water. As before, the compound was extremely soluble in water except in the presence of chloride ions, and analytically pure specimens were difficult to obtain. The substance was easily soluble in alcohol or acetone, and with alcoholic silver nitrate precipitated part of its chlorine in the cold, and the rest on heating. Finally, metallic silver was deposited. Treatment of the aqueous solutions with potassium iodide or bromide gave precipitates of probably chloro-pentakispyridine rhodous iodide and bromide.

Found: Rh, 18·3%; Cl, 13·2%. Calculated for $(Rh(C_5H_5N)_5Cl)Cl$: Rh, 18·08%; Cl, 12·48%.

Bis-pyridinium tetrachloro tetrakis-pyridine μ *dichlorodirhodium.* This substance, which is the chlorine analogue of (VII), was prepared by refluxing the pentakis compound (0·8 g.) with 1 N. hydrochloric acid (30 mls.) and a few drops of hypophosphorous acid in an atmosphere of carbon dioxide. The yellow solution after a short time deposited a mass of fine pinkish buff needles which were washed with dilute hydrochloric acid in which they were completely insoluble. The substance was also insoluble in benzene and chloroform and very slightly soluble in hot alcohol. With alcoholic silver nitrate on heating, a precipitate of silver chloride was obtained followed by metallic silver. In the preparation of this compound, which involves the removal of three pyridine molecules from the pentakis compound, despite a great many attempts it has not been possible to stop the reaction at the stages represented by the tetrakis or tris pyridine compounds. If the reaction were stopped when only part of the pyridinium salt was precipitated, and the filtrate cooled, it always contained unchanged pentakis compound.

Found: Rh, 23·04%; Cl, 23·8%. Calculated for $(C_5H_5N.H)_2(Rh_2Cl_6(C_5H_5N)_4$: Rh, 23·02%; Cl, 23·8%.

Tetrakis-pyridinium hexachloro bis-pyridine μ *dichlorodirhodium.* This substance, the chlorine analogue of (VIII), was obtained from the filtrate of the previous preparation or by carrying on the reaction with hydrochloric acid until the bis-pyridinium salt had almost dissolved. On cooling the red solution, it deposited bright reddish orange needles, which were washed with dilute hydrochloric acid, and finally to prevent loss of chlorine, with 0·1 N. hydrochloric acid. The substance was slightly soluble in alcohol and acetone, and reduced alcoholic silver nitrate to the metal. By treatment of the compound for an hour with hydrochloric acid, it gave a water-soluble compound, which is probably the chlorine analogue of compound (IX).

Found: Rh, 21·6%; Cl, 29·7%. Calculated for $(C_5H_5N.H)_4(Rh_2Cl_8(C_5H_5N)_2)$: Rh, 21·23%; Cl, 29·34%.

Hexakis-pyridine rhodous iodide. Rhodium trichloride solution (10 mls.), containing 0·09 g. rhodium, was treated with potassium iodide (5 g.) and water (10 mls.). The mixture was heated to form the deeply coloured potassium iodorhodite, and then treated with pyridine (15 mls.), followed by 30% hypophosphorous acid (2 mls.). The mixture was refluxed in an atmosphere of carbon dioxide until it became pale yellow in colour, and a slight precipitate of rhodium metal had come down. The solution was then filtered in an atmosphere of carbon dioxide, and cooled in the same atmosphere to 0° C. The glistening pale yellow rhombs belonging probably to the rhombic system, were filtered in an atmosphere of carbon dioxide and washed with oxygen-free 30% aqueous pyridine solution. The substance was finally dried over sulphuric acid in an inert atmosphere. The compound lost pyridine immediately by washing with water, and was transformed into the more insoluble pentakis compound. It rapidly oxidised in the presence of oxygen to the dark purple rhodic compound, which however was easily soluble in aqueous pyridine. The pure hexakis compound was readily obtained by dissolving the pentakis compound (see later) in pyridine in the presence of hypophosphorous acid and cooling in ice in the presence of carbon dioxide.

The substance was easily soluble in alcohol or acetone, and precipitated the whole of its iodine by treatment with silver nitrate, which was reduced to the metal on heating.

Found: Rh, 12·6%; I, 31·2%. Calculated for $(Rh(C_5H_5N)_6)I_2$: Rh, 12·39%; I, 30·56%.

Iodo-pentakis-pyridine rhodous iodide. This substance was prepared as for the hexakis compound above, except that the filtrate, after cooling in ice, was treated with cold freshly reduced constant boiling hydriodic acid (15 mls.), the solution warmed to 30° C. and then cooled again in

ice. The pale yellow microcrystalline precipitate was filtered in an inert atmosphere, and washed several times with oxygen-free ice cold water. The substance was easily soluble in hot water, and crystallised out again on cooling. It was also readily soluble in alcohol, in which alcoholic silver nitrate precipitated part of the iodine at room temperature, and the remainder, with reduction to metallic silver, on heating. The substance readily oxidised in the air, becoming brown.

Found : Rh, 13·9% ; I, 33·6%. Calculated for $(Rh(C_5H_5N)_5I)I$: Rh, 13·69% ; I, 33·78%.

The effect of hot acids or hypophosphorous acid on iodo-pentakis-pyridine rhodous iodide. In attempts to prepare other pyridine coordinated compounds with rhodous iodide, the usual procedure of boiling with decolourised hydriodic acid was carried out. This resulted, however, in the evolution of large volumes of hydrogen gas, and the formation of black insoluble precipitates of variable composition. Substitution of a mixture of hydrochloric acid and potassium iodide for hydriodic acid, and the use of sulphurous acid in lieu of hypophosphorous acid to keep the substance reduced, also gave no satisfactory results. Finally, bromo pentakis rhodous bromide was dissolved in water, which had been boiled free of oxygen, treated with potassium iodide and a little hydrochloric acid, and heated to boiling. Apart from the production of iodo pentakis rhodous iodide, which came down on cooling, no reaction occurred. Addition of hypophosphorous acid, however, instantly caused the formation of a deep purplish precipitate, and the evolution of hydrogen gas. Continued boiling then dissolved the purple precipitate, and from the pale yellow solution no compound could be isolated.

The purplish precipitate was variable in composition, insoluble in alcohol, but reduced alcoholic silver nitrate to the metal. As a result of the analyses, a possible formula $Rh_2(C_5H_5N)_5I_5$ is suggested.

Found : Rh, 16·6%, 17·7% ; I, 50·84%, 53·8%. Calculated for $Rh_2(C_5H_5N)_5I_5$: Rh, 16·65% ; I, 51·39%.

Summary.

The reduction of hexakis pyridine rhodic halides by hypophosphorous acid in the presence of excess pyridine has been found to yield the corresponding hexakis pyridine rhodous halides as yellow crystalline solids. By treatment with acids the pyridine molecules can be successively removed to yield other pyridine coordinated compounds. Practically the whole series, from the hexakis compound to the pyridinium salts, have been obtained with rhodous bromide, but owing to unsuitable solubility relationships, or extreme ease of oxidation, various compounds in the series with rhodous chloride and iodide are missing.

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A NOTE ON THE MAGNETIC BEHAVIOUR OF POTASSIUM CYANONICKELITE.

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Monovalent nickel (Ni^I) is isoelectronic with bivalent copper and should therefore exhibit, in its compounds, a paramagnetic susceptibility consistent with the existence of one unpaired electron spin. Some time ago Szegö and Ostinelli (1930) reported that potassium cyanonickelite is diamagnetic, a finding which is contrary to the above prediction. Because of this deviation from predicted behaviour and because of the meagre experimental detail given by Szegö and Ostinelli, it was thought worth while to reinvestigate the compound. An added reason is to be found in the recent work of Eastes and Burgess (1942) who, for the first time, isolated pure specimens of solid potassium cyanonickelite and definitely established its composition as K_2NiCN_3 (and not K_3NiCN_4). Some difficulty is experienced in working with the cyanonickelite owing to the extraordinary ease with which it undergoes oxidation. It was found most convenient in the present work, to deal with aqueous solutions.

Experimental.

A solution of potassium cyanonickelate was made up to contain 0·02346 g. Ni/ml ; 25 ml. of this solution were reduced with sodium amalgam containing 1 g. of sodium. The whole was vigorously shaken during the reaction and when reduction had ceased a 10 ml. sample was withdrawn for analysis ; a second sample was immediately used for a determination of its susceptibility by the Gouy method. It is important to note that reduction was never, at any time, complete.

Method of Analysis. A 10 ml. sample of the reduced solution was poured into 25 ml. of ammoniacal silver nitrate solution and the resulting black precipitate of silver washed with ammonia, sodium thiosulphate and water ; it was then dried and weighed. The corresponding weight of Ni was used to calculate the percentage conversion of Ni^{II} to Ni^I.

Results. From the tube constant and other data it was calculated that, in the most favourable instance (case B in table below), a change in $\Delta\omega$ of the order of $+10$ mgm. would have been observed had K_2NiCN_3 become paramagnetic with Ni^I possessing one unpaired electron spin. No such change in $\Delta\omega$ was observed ; oxidation and reduction produced very little change in the susceptibility of the various solutions as shown in the accompanying table.

Analysis of Results.

Solution.	Susceptibility of the Solution.
A. Containing 0·0116 g. Ni^I/ml. representing 49·5% conversion of Ni^{II} to Ni^I	$-0{\cdot}66\times10^{-6}$
B. Containing 0·0170 g. Ni^I/ml. representing 72% conversion	$-0{\cdot}65\times10^{-6}$
C. Containing 0·0119 g. Ni^I/ml. representing 51% conversion	$-0{\cdot}66\times10^{-6}$
D. Blank solution	$-0{\cdot}68\times10^{-6}$
E. Oxidised solution (C, above)	$-0{\cdot}65\times10^{-6}$

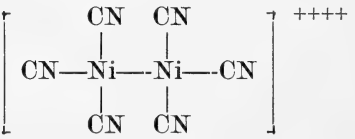
The blank solution referred to contained $K_2Ni(CN)_4$ (0·02346 g. Ni/ml) and NaOH, the latter at the same concentration as in A, B and C. The oxidised solution was obtained by bubbling air through a reduced solution until all the typical deep red colour had disappeared.

Discussion.

From the above it may be inferred that K_2NiCN_3 is diamagnetic with a susceptibility not very different from that of K_2NiCN_4. The finding of Szegö *et al.* (1930) is thus confirmed. The observed diamagnetism may mean either

(1) that there is no unpaired electron spin to be observed, or
(2) that the unpaired electron spin exists but is quenched because of some inter- or intra-atomic interaction.

As there are no theoretical grounds for believing that the second suggestion is correct, the first is adopted. It can be reconciled with the prediction made earlier, by postulating a structure involving a metal-metal bond :



In the formation of the metal-metal bond the odd electron on each metal atom is paired up. Precisely the same kind of bond is formed in mercurous chloride (Hg_2Cl_2) ; but for formation of the Hg-Hg bond, mercurous chloride would be paramagnetic. Further instances of metal-metal bonds could be cited but one other must suffice.

Recent electron diffraction studies (Davidson *et al.*, 1940) have revealed the presence of a metal-metal bond in aluminium trimethyl $Al_2(CH_3)_6$. There would seem to be no inherent reason, then, why such a bond should not occur in the cyanonickelite ion. This explanation of the diamagnetism of the ion has the additional advantage of giving Ni^{I} a coordination number of four which is the number one would anticipate from a comparison with isoelectronic Cu^{II}. From the same comparison it is highly probable that the complex ion $[Ni_2CN_6]^{----}$ has a planar structure with Ni^{I} forming dsp^2 bonds.

References.

Eastes, J. W., and Burgess, W., 1942. *J. Amer. Chem. Soc.*, **64**, 1187.

Davidson, N. R., Hugill, J. A. C., Skinner, H. A., and Sutton, L. E., 1940. *Trans. Far. Soc.*, **36**, 1212.

Szegö, L., and Ostinelli, P., 1930. *Gazz. Chim. Ital.*, **60**, 946.

FUNCTIONAL RELATIONS BETWEEN SCROTUM AND POUCH AND THE EXPERIMENTAL PRODUCTION OF A POUCH-LIKE STRUCTURE IN THE MALE OF *TRICHOSURUS VULPECULA*.

By Adolph Bolliger, Ph.D.

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(With Plates XVI-XVIII.)

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Introduction.

Edward McCrady, Jr. (1939), in his book on the embryology of the opossum (*Didelphys virginiana* Kerr) states that the perfect parallelism between the development of the scrotal anlagen and the lips of the pouch makes it impossible for him to avoid the conclusion that the lips of the pouch represent the labia majora, the homologues of the scrotum in higher mammals. To this statement, however, he adds that this homology has never been suggested before, though a number of investigators have studied the development of the pouch and the descent of the testes, which suggests that there must be some obvious and fundamental objection to it, though McCrady confesses that he has been unable to think of any such objection.

On the other hand, Abbie (1941) in his recent paper on " Marsupials and the Evolution of Mammals " states that essentially the pouch is formed by an insinking of the mammagenous skin of the ventral abdominal wall through a gap in the underlying cutaneous musculature. The sole peculiarity in connection with the pouch according to this author is the hiatus in the musculature which permits insinking of the mammagenous zone and the reader is left with the impression that the homologous organ in the male would be the mammary glands or nipples if any were present.

Studies in this laboratory on the response of the scrotum and the pouch of the diprotodont marsupial *Trichosurus vulpecula*, the common Australian phalanger or possum, have furnished a number of functional results which have a direct bearing on this subject. Some of these findings have already been published in connection with other problems, but many more recent experimental observations necessitate a summary of the situation which will be given under the following headings :

(1) Anatomical considerations.
(2) Materials.
(3) Response of scrotum and pouch to testosterone propionate, an androgen.
(4) Response of scrotum and pouch to progesterone.
(5) Response of scrotum and pouch to gonadotropin obtained from pregnancy urine.
(6) Response of scrotum and pouch to œstrogens.
(7) Eversion of pouch in untreated females.

(1) Anatomical Considerations.

This paper deals with reactions of a skin area located on the lower abdomen of *Trichosurus vulpecula*, in which in later life scrotum and pouch are formed and which will be referred to as the scroto-marsupial area. In contrast to the abdominal region in general this area is characterised by the presence of only little skin muscle as shown by histological examination and electrical stimulation experiments. In the fully developed animal this area is further characterised by the sparseness of hair growth as compared with the rest of the abdomen.

A few days after birth paired lateral swellings or ridges arise in this area. They are the first indication of the future pouch and scrotum. In the case of a male these swellings soon begin to fuse at the caudal end and a hemispherical extrusion is formed which is the beginning of a definite scrotum. As the scrotum increases in size the lateral swellings fuse completely to form ultimately the large sac and neck of this organ.

In the case of a female the lateral swellings fuse only inferiorly, and not an extrusion as in the case of the male, but an invagination of skin takes place beneath the point of fusion. This invagination or infolding takes place also laterally along the ridges. Fusion except at the caudal end does not occur, but in order to form a practically closed pouch the original swellings which now represent the lips of the pouch approximate along the mid-line. In *Trichosurus vulpecula* as well as in other marsupials the skin musculature, as pointed out before, extends into the lips of the pouch, where its fibres are present in such increased numbers as to justify their separate name " sphincter marsupii ", as distinct from the panniculus carnosus in general. The skin lining the pouch itself contains only few muscle fibres, as does the scrotal sac.

From the anatomical development it would follow that the scrotum is an extrusion of the " sexual " skin constituting the scroto-marsupial area and that the pouch is an invagination of it. In the male this extrusion of skin, the scrotum, houses the testes ; in the female the mammary glands become situated in the posterior wall of this invagination which is commonly referred to as the pouch.

This arrangement again becomes evident if we consider the cremaster muscles in the two sexes. In the male they pass right into the interior of the scrotum, while in the female they do not penetrate the pouch wall.

(2) Materials.

In a previous communication (Bolliger, 1940) it has been mentioned how to capture possums and how to keep them in captivity. The technique of measuring the capacity of the pouch in the female has also been reported (Bolliger, 1942).

The sex hormones used in this investigation were all administered subcutaneously or intramuscularly. They were obtained in the form of the following commercial preparations : Perandren (Ciba), a solution of testosterone propionate in sesame oil ; Lutocyclin (Ciba), an oily solution of progesterone ; Gonan (B.D.H.), the dry gonadotropic substance obtained from human pregnancy urine which was dissolved in water prior to injections ; Stilbœstrol (B.D.H.), an oily solution of diethylstilbœstrol ; Ovocyclin (Ciba), an oily solution of œstradioldipropionate.

(3) Response of Scrotum and Pouch to Testosterone Propionate, an Androgen.

As pointed out in a previous communication (Bolliger and Carrodus, 1940*c*), in sexually immature animals these organs showed a pronounced response to the administration of testosterone propionate. For example, in a male pouch young

of about $3\frac{1}{2}$ months of age as well as in a male of about 10 months of age, the scrotum became markedly elongated as compared with untreated males. In females of about similar age the pouch also developed precociously. It rapidly increased in size and the lips became thickened. But in spite of sustained injections the increase in size of pouch as well as scrotum was only temporary and was followed by a marked decrease in size which amounted almost to atrophy.

In general these experiments indicated that pouch and scrotum responded in a similar manner towards the administration of testosterone propionate.

(4) Response of Scrotum and Pouch to Progesterone.

Progesterone, the action of which is mainly concerned with the change of the uterine endometrium during the menstrual cycle and pregnancy has also a definite influence on the pouch as shown on a previous occasion (Bolliger and Carrodus, 1940*b*). The administration of progesterone to young or fully grown females brought on a relaxation of the pouch after a preliminary enlargement and the lips became separated.

The injection of progesterone into fully grown males gave no definite results but in adolescent animals a broadening and relaxation of the neck of the scrotum was noticed. This broadening made it possible to push the fully developed testes readily out of the scrotum, while in the untreated animal of similar age it was impossible for them to leave the scrotum on account of the presence of a far too narrow scrotal neck (Bolliger and Carrodus, 1939*a*). These experiments seem to indicate that progesterone possesses a relaxing and broadening property which makes itself manifest on the tissues of the pouch as well as on those of the scrotum.

(5) Response of Scrotum and Pouch to Gonadotropin obtained from Human Pregnancy Urine.

Recently it has been shown (Bolliger, 1942) that gonadotropin obtained from pregnancy urine brings on an enlargement of the pouch after a preliminary short-lived contraction. With large doses the enlargement may be as much as 20 times measured on the capacity of the organ.

In previously unpublished experiments it was noted that in the fully grown male an elongation of the neck of the scrotum took place after the administration of chorionic gonadotropin. But the results were not spectacular, amounting to a maximum elongation of about 1 cm. In the young animal of about 4–6 months of age after the administration of gonadotropin the scrotum was found to be as much as four times the size of that of untreated males. It was further observed that such an enlargement was independent of the presence of the testes and epididymes because after their removal the empty scrotal sac became even more markedly enlarged following further injections of gonadotropin.

Comparing the experimental results obtained from the administration of gonadotropin one may again state that both scrotum and pouch responded similarly, there being a large expansion in each case.

(6) Response of Scrotum and Pouch to Œstrogens.

The response of the scroto-marsupial area to œstrogens can be divided into three phases :

(*a*) Swelling.

(*b*) Contraction.

(*c*) Formation of a pouch-like structure in males.

(a) Swelling.

Twenty-four hours after the injection of about 0·3 mg. or more of œstrogen (stilbœstrol, œstradioldipropionate, etc.) into adolescent or fully grown males, a swelling of the scrotum was noticed. The fairly thin scrotal skin as seen in the untreated animal became thickened, giving it a felt-like texture. Particularly in adolescent animals or after repeated injections this swelling was sometimes so marked as to alter the typical heart-shaped outline of the scrotum into that of a round or a plum-shaped body. A swelling of the abdominal skin surrounding the scrotal stalk was also noticed. Then within a week or two after the last injection the swelling subsided and provided a sufficiently large amount of œstrogen had been administered the phase of contraction became very noticeable.

In the female a similar swelling of the skin of the pouch and of the tissue surrounding it was noted after the administration of œstrogen. Externally this was first observed in the lips of the pouch, which became thickened (Bolliger and Carrodus, 1940*a*).

As far as the interior of the pouch was concerned the swelling was short-lived only, i.e. one or several days, and it passed almost imperceptibly into a contraction of this organ. There is little to hinder this as in contrast to the scrotum the pouch is essentially an empty structure.

Otherwise the swelling as observed in the scroto-marsupial area after the administration of œstrogen was similar in nature in males and females. In both sexes after it had subsided it could be reproduced again by a subsequent injection of œstrogen. This was also the case when a high degree of contraction was already present.

(b) Contraction.

In the female one of the first external signs indicating that the process of contraction had begun was a puckering of the swollen lips. In addition, the interior of the pouch itself contracted markedly. For example, a pouch which in its pre-experimental and resting stage had a capacity of about 5 ml. of water, showed two weeks after the injection of 2–5 mgs. of an œstrogen, such as œstradioldipropionate, no capacity due to the rigid apposition of its anterior and posterior walls and its depth was only about 0·3–0·4 cm. in contrast to the pre-experimental depth of 3–4 cm. This was accompanied by a thickening of the skin musculature situated in and near the lips of the pouch (Bolliger and Carrodus, 1940). This contraction, however, was not permanent and within a few weeks the pouch began to expand again (Bolliger and Carrodus, 1940*a*).

In the male the first sign of contraction was a shortening of the scrotal neck. This was followed by a diminution in size of the testes together with a somewhat corresponding amount of scrotal contraction. The next step in the process was that of the ascent of the testes, which ultimately led to an emptying of the scrotum. The scrotal sac now not only collapsed, but actually disappeared to a large extent. For example, in a fully grown animal in which testicular ascent had taken place only a small area or a small heap of wrinkled skin remained where previously a large pendulous scrotum was present (Bolliger and Carrodus, 1939 ; Bolliger and Canny, 1941).

In the work published so far, testicular ascent and complete scrotal collapse was only accomplished in immature males, while in fully grown animals where this process required more intensive treatment only partial ascent was obtained. This was mostly due to the fact that frequent injections were repeated at weekly intervals till the animal became moribund. However, in recent experiments it has been found that complete ascent could also be readily obtained in sexually mature males when the injections were stopped before a lethal dose had been administered. Complete testicular ascent and scrotal collapse were observed in two sexually mature males about five to six weeks after the last injection of œstrogen. Approximately after another month the scrotum began to reform

and the testes to descend as described previously in the case of younger animals (Bolliger and Canny, 1941).

Again a marked similarity in response by scrotum and pouch towards œstrogens could be observed during the stage of contraction and restoration. The next chapter, however, deals with an effect which necessarily is confined to males only.

(c) Formation of a Pouch-like Structure in Males.

On both sides of the collapsed scrotum a semilunar fold appeared which suggested the formation of a rudimentary pouch. However, the nature of these folds was not quite clear because usually they became very prominent only when the animal wilfully contracted the lower region of the abdomen, which took place, for example, on stroking the scrotal region. Furthermore, these folds disappeared a few weeks after the injection of œstrogen was stopped when the scrotum began to reform.

In order to obtain a more definite and if possible a permanent formation of the semilunar folds, testicular ascent and scrotal collapse were produced several times in succession in the same immature animal. A male of eight months of age (Experiment 201) was given by subcutaneous injection a total of 7 mg. of stilbœstrol in a series of five injections over a period of four weeks. Testicular ascent and scrotal collapse were present after terminating the injections. The semilunar folds had also developed, but they became more marked a fortnight after terminating the injections. During the four weeks following the greatest development of the folds the scrotum began to reform again and the folds became less prominent. At this stage a series of fresh injections of stilbœstrol was given and the folds reformed again. This process was repeated three times and it was found that the folds produced at the third series of injections were somewhat more pouch-like than those observed after the first series of injections. This applied particularly to the depth and to the infolding of the lateral wall of the pouch formed (Plate XVI, Fig. 1). That is to say, the animal was capable of contracting its skin muscles in such a manner as to form a hollow indentation of about 3 cm. in diameter and of maximum depth of 0·5 cm. around the scrotal remnant. The skin fold forming the margin of this indentation was overhanging the lateral part of the floor of the hollow and a definite recess whose greatest lateral extent was 0·3 cm. was formed.

When the animal relaxed, this pouch-like structure became less distinct. In addition, it disappeared almost completely a month or two after the last injection, when the scrotum had completely reformed and the testes had descended. However, a slightly raised ridge due to some thickening of the skin muscle remained permanently.

In subsequent experiments an attempt was made to obtain a more permanent " pouch " by removing the testes by operation. But the results with an animal of eight months of age in which the testes were removed through an incision in the scrotal sac were essentially the same as those obtained in the experiments already mentioned. After the injections of œstrogen the scrotum collapsed and contracted and marked folds appeared laterally to it, but a complete inversion so far did not take place and a scrotal remnant of about 0·7 cm. in width was still present between the folds seven weeks after the first injection of œstradioldipropionate.*

The skin lining the pouch of sexually mature and maturing *Trichosurus vulpecula* sometimes secretes a characteristic reddish brown pigment, the appearance of which has been observed in connection with the sex life of the untreated animal and after the injection of œstrogen. In the experiments just mentioned a similar reddish-brown pigment was seen to appear on several

* Six months later on, however, the scrotal remnant had disappeared and a permanent pouch had formed. (Added in proof).

occasions on the skin lining the pouch-like cavity formed after the administration of œstrogens to males.

Though the tendency of the skin to form a fold between panniculus carnosus and abdominal musculature was obvious after the administration of œstrogen a true pouch-like structure had not been obtained because so far a remnant of the scrotum refused to invert. Therefore, it seemed necessary to resolve the scrotum into its original bifid structure in order to obtain complete inversion. For such an experiment it also seemed advantageous to choose pouch young of only a few months of age.

Consequently the small scrotal sac of four pouch young of $2\frac{1}{2}$ to 4 months of age was amputated with or without the testes and it was hoped that this operation would prevent the now separated scrotal ridges from fusing together again in the process of subsequent development. Œstradioldipropionate in comparatively large doses was then administered. In addition these pouch young were given injections of gonadotropin obtained from pregnancy urine because it had been shown that this substance brought on an extension of the pouch in the female (Bolliger, 1942), and because the impression had been gained that this gonadotropin afforded some protection against the toxic action of the œstrogen.

The youngest animal used in this series (Y223) aged $2\frac{1}{2}$ months died before pouch proper had developed. Due to the epithelial hyperplasia and keratinization in the urogenital sinus as produced by the œstrogen, urinary obstruction developed and consequently the bladder became distended with urine and took on huge dimensions which led to the death of the still hairless pouch young.

In two older pouch young of four months of age (Y222, Y218) the scrotum was amputated together with the testes, which by now were lodged completely in the scrotum. Prior and immediately after the operation these animals were given chorionicgonadotropin. A few weeks after the removal of scrotum and testes œstradioldipropionate was administered in amounts of 0·1 to 0·2 mg. In both of these animals urinary obstruction below the bladder and consequent bladder distension were also met with. In order to prevent the animals from dying from this enormously distended bladder, the bladder was grasped through the abdominal wall and compressed till urine began to flow out from the urethral opening. This procedure was repeated almost daily and the animals were kept in a fair measure of health for about two months from the beginning of the injections. Already after one month from the date of the first injection of œstrogen a typical pouch had formed which, however, still showed some imperfections. In one instance (Experiment Y222) the lips had developed as in a normal pouch and infolding had taken place along them and particularly at the caudal end; but no apposition of the lips was obtained. They formed a V-shaped figure with an internal angle of about 60° which persisted up to the death of the animal and which was somewhat similar to the arrangement of the lips of the pouch as seen in untreated females of about three months of age (Plate XVI, Fig. 2).

In the other animals the lips of the experimentally produced pouch (Experiment Y218) were parallel and they nearly approached each other, leaving only a space of about 0·4 cm. between them (Plate XVII, Fig. 1). The anteroposterior depth of the pouch was considerable, i.e. 0·4 cm., and there was infolding of the skin along the almost closed lips with the exception of the caudal end of this experimentally produced marsupium. These and other imperfections as met with in these two experiments were possibly due to the removal of too much of the elements required for the formation of the pouch during the extensive operation of amputating the developing scrotum containing the testes. Such an operation, of course may mean that elements required for the formation of the pouch were removed.

This was probably borne out by the fact that the best result was obtained from a pouch young of three months of age (Experiment Y211) in which the testes occupied a position external to the body wall but had not yet entered the scrotal sac. About two-thirds of the small scrotum so far formed, i.e. 0·2 cm., was amputated with the testes left behind. Following this small operation the scrotum regained its original bifid structure and retained it throughout the experiment. A fortnight after the amputation 40 I.U. of gonadotropin were injected and a month after the operation 0·2 mg. of œstradioldipropionate was administered. A second and third injection of 0·2 mg. of œstradioldipropionate were given respectively one week and three weeks later. Already after the first injection of œstradioldipropionate a V-shaped ridge of raised tissue formed by the remaining scrotal elements and containing the separated testes became very prominent. After the second injection of œstradioldipropionate definite infolding of the abdominal skin along this ridge became visible and a recess was formed beneath it. A typical pouch had formed but its swollen and puckered lips were still diverging cephalad at an angle of about 45°. After the third injection of œstradioldipropionate the animal was capable of closing the lips almost completely, thus presenting a fully developed pouch similar in size and shape to that found in females of about equal age treated with œstrogens (Plate XVII, Fig. 2). The small and elongated testes remained situated in the lips of the pouch and were not discernible on superficial examination. The body weight of the animal was at this stage 260 g.

These three animals lived for about another month after the pouch had been established, then they all died, apparently from some toxic effect of the administered œstrogen.

Histological Examination.

The whole of the animal (Experiment Y218) was hardened in formalin and transverse sections of the lower abdominal wall, where the artificial pouch was situated, were prepared. As shown in Plate XVIII, Fig. 1, the experimentally produced pouch was a deep indentation in the subcutaneous tissue with a marked tendency to lateral infolding. The skin muscle was extended into the lips of the pouch and was thickened in this region. Lateral to the pouch were situated the inguinal glands, which were enlarged. The broadening of the subcutaneous tissue was an outstanding change from the normal and made it possible for the skin to sink into a maximum depth of about 0·3 cm. and to form this pouch. The enlarged inguinal glands also seemed to play an important part in the formation of this broad subcutaneous band of areolar tissue which was found to be absent in the region above the pouch.

(7) Eversion of Pouch in Untreated Females.

On this occasion an example may be given to illustrate the fact that the pouch of a female may become an everted pendulous structure just like the scrotum in males. This refers to a female who was still nursing a young of about six or seven months of age. As frequently seen in such cases, the mammary gland from which the young was feeding took on such large dimensions as to protrude through the lips of the pouch and force the pouch to prolapse or revert completely. The picture thus obtained was that of a spherical mass containing the enlarged mammary gland of about 6 cm. in diameter suspended on a thin neck of about 3 cm. in length and resembling, on superficial examination, a large scrotum (Plate XVIII, Fig. 2). After the nursing young was removed from its mother, the enlarged mammary gland regressed and ultimately regained its normal size and simultaneously the pouch reformed.

Discussion.

As already pointed out in the experimental part of this paper, the reactions of scrotum and pouch towards testosterone, progesterone and gonadotropic hormone are similar in many respects and they will support claims of homology between these organs which have been made on anatomical grounds. The experiments with œstrogens supplied further functional evidence of this homology and ultimately they furnished a means of transforming one of the two organs, the scrotum, into a typical pouch-like structure. However, it has to be emphasised that the homology is between the whole of the pouch structure and the whole of the scrotal sac and not as stated (McCready, 1938) between the lips of the pouch and the scrotum. Therefore if we accept the general assumption that the labia majora are the homologue of the scrotum in higher mammals, then the pouch itself together with its lips necessarily becomes the homologue of the labia majora.

The extensively studied reactions with œstrogens have been subdivided into three stages. The first stage, that of swelling, may be considered as one of stimulation and may be compared with the swelling of the " sexual skin " at the hind ends of the body of primates after the administration of œstrogens.

The second stage, contraction, may be considered primarily an atrophy similar to that seen in mammals in general after the administration of sufficiently large quantities of œstrogens. These large doses abolish the secretions from the pituitary gland and reproduce to a large extent the picture as seen after hypophysectomy. Ovaries and testes atrophy and with them all the other sex organs. In our phalanger the atrophy of the testes is marked after the administration of œstrogens. Then the testes leave the scrotum and the scrotum itself shrivels up. A similar process takes place in the female, where the ovaries atrophy and the pouch contracts.

Several causes may be responsible for the formation of the pouch-like folds in intact males both during and subsequent to the period of contraction. When examined immediately after their appearance, these folds could be explained as being due to traction by the fibres of the cremaster muscle on the testes on the one hand, and traction on the inguinal glands on the other (Bolliger and Carrodus, 1939*b*). This mechanical factor certainly may iniate these folds, but it is by no means indispensable because after severing the connection of the cremaster with the testes as in those experiments where scrotum and testes or the testes alone had been removed, marked pouch-like structures were produced after the administration of œstrogens. Undoubtedly the process is much more complex, and particularly in younger animals the following reactions occur in conjunction with the contraction of the scrotum and the insinking of the sexual skin of the scroto-marsupial area as brought on by œstrogens. The skin musculature in this area thickens markedly as in females. The subcutaneous areolar tissue near the folds becomes very broad and the so-called inguinal glands increase in size. All these reactions are due to stimulation, which may be directly exerted by the œstrogen on the scroto-marsupial area because they take place in the absence of the testes.

In order to obtain a more definite pouch in males it seemed, as already pointed out, to be necessary to prevent the scrotal primordia from fusing or if they had already fused to effect some kind of a separation into a bifid structure. Efforts along these lines led to a certain measure of success. By removing beforehand the tip of the future scrotum in pouch young of three to four months of age, and after the injection of œstrogens a structure was produced which has the characteristics of a diprotodont marsupium. Thus the anatomical assumption that the scrotum is an extrusion of the sexual skin constituting the scroto-marsupial area and the pouch an invagination of it has been proven in the conversion of the scrotum into the pouch. *Vice versa*, it has not been attempted

yet to produce from the pouch in females a scrotum by experimental methods, but observations have been made on pouches of fully grown animals which were spontaneously converted into a scrotum-like structure by prolapse of an enlarged mammary gland.

So far, only such temporary eversions of the pouch have been observed and congenital abnormalities of a permanent nature relating to the homology of pouch and scrotum have not been met with in the diprotodont *Trichosurus vulpecula*. However, in the male polyprotodonts *Chironectes panamensis* and *Thylacinus cynocephalus*, there occurs a pouch-like structure around the scrotal neck (Enders, 1937).

The animals which were operated upon also received injections of chorionic gonadotropin for reasons mentioned. It is not certain, however, whether these injections materially influenced the course of the experiments. Unfortunately this group of animals did not survive the formation of the pouch for more than about one month. It is hoped, however, that in future it should be possible to obtain longer survival periods by giving smaller doses of œstrogen.

The sensitivity towards œstrogens is most marked in the region of the urogenital sinus which includes the prostatic urethra. Enormous hyperplasia and metaplasia in this region lead to urinary obstruction (Carrodus and Bolliger, 1938) which, however, can be corrected to a certain extent by compressing the distended bladder.

In the past, scrotum and pouch have been looked upon mainly as containers of testes, mammary gland and offspring, respectively. The observations recorded in this paper emphasise to no small extent the active rôle of scrotum and pouch as individual sex organs though coordinated with the needs of testes, etc., under normal conditions. Under experimental conditions it can be shown that, for example, a pouch may be produced in a male in the absence of mammary glands and ovaries by the administration of sex hormone which, in the case of stilbœstrol, has not even a chemical connection whatsoever with hormones occurring in the animal body.

It seems that the animals must reach a certain degree of scrotal development before they respond satisfactorily to œstrogens. So far, only in animals of about three months of age has it been possible to obtain a pouch-like structure while in generic males of one to two months of age, which presented about the first sign of a developing scrotum, the administration of œstrogen did not bring on scrotal atrophy and pouch formation at that age. This may explain why Burns (1939) and Moore (1941) in their work on the action of œstrogens on pouch young of the American opossum, *Didelphys virginiana*, up to a maximum age of three months, did not observe any effect on the scrotum or the pouch. Another possible explanation, however, would be that the polyprotodonts such as *Didelphys virginiana* respond differently from diprotodonts such as *Trichosurus vulpecula*.

Finally, it may be stated that probably so far, no other organ in a mammal after birth has been more successfully converted into its homologue of the opposite sex than the scrotum into the pouch in the three to four months old phalanger. This statement also includes the experiments on a newly born, sexually undifferentiated, pouch young of *Didelphys virginiana* in which modification of sex organs was very marked but conversion of sex organs hardly met with.

Of course, other organs such as the penis were altered simultaneously with the scrotum by the administration of œstrogen, but a discussion of these changes does not fall within the scope of this paper. Many other questions have also been opened up in connection with this experimental study on the scrotum which may require some attention at a future date. For example, there is the question

as to the nature of the subsequent development of the scrotum after amputation of its tip, which is followed by the administration of sex hormones other than œstrogens.

Summary.

Scrotum and pouch are found to behave in a similar manner in their response to sex hormones.

Testosterone propionate brings on a development, progesterone a relaxation, and chorionic gonadotropin a marked extension of both these organs.

Œstrogens bring on swelling and then contraction of both scrotum and pouch, but in addition temporary folds begin to form on both sides of the scrotum which, particularly in young animals in which they had been brought on repeatedly, suggest strongly the formation of a pouch, though some remnant of the contracted scrotum always remains between them.

A pouch-like structure without a scrotal remnant was produced by amputating the tip of the developing scrotum in males of 3 to 4 months of age, the amputation being followed by the administration of œstrogens.

All the experiments described in this paper indicate and finally prove that the scrotum is an eversion, and the pouch an invagination of the scroto-marsupial area and that consequently on functional grounds they are homologues.

Complete prolapse of the pouch and formation of a pendulous mammary gland similar in appearance to a scrotum was observed in a nursing female.

References.

Abbie, A. A., 1941. *Aust. J. Sc.*, **4**, 1.
Bolliger, A., 1940. *Aust. J. Sc.*, **3**, 59.
Bolliger, A., 1942. This Journal, **76**, 137.
Bolliger, A., and Canny, A. T., 1941. This Journal, **75**, 21.
Bolliger, A., and Carrodus, A., 1939*a*. *Nature*, **144**, 671.
Bolliger, A., and Carrodus, A., 1939*b*. *Austral. and N.Z. J. Surg.*, **9**, 155.
Bolliger, A., and Carrodus, A., 1940*a*. This Journal, **73**, 218.
Bolliger, A., and Carrodus, A., 1940*b*. This Journal, **73**, 228.
Bolliger, A., and Carrodus, A., 1940*c*. *Med. J. Austr.*, 368.
Burns, R. K., 1939. *J. Morph.*, **65**, 497.
Carrodus, A., and Bolliger, A., 1939. *Med. J. Aust.*, 1118.
Enders, R. K., 1937. *J. Morph.*, **61**, 1.
McCrady, E., Jr., 1939. The Embryology of the Opossum. Wistar Institute, Philadelphia, p. 199.
Moore, C. R., 1941. *Physiological Zoology*, **14**, 1.

Explanation of Plates.

Plate XVI.

Fig. 1 (Experiment 201).—Photograph showing the folds lateral to the collapsed scrotum following the repeated administration of œstrogen. Present age of phalanger is approximately one year. Note the depth of the pouch-like structure and the infolding of the lateral wall.

Pictures of a normal and a treated but restored scrotum are given in previous publications (Bolliger and Carrodus, 1939*b*, and Bolliger and Canny, 1941).

Fig. 2 (Experiment Y222).—Photograph showing condition of experimentally produced pouch in a young male of approximately $5\frac{1}{2}$ months of age. The picture was taken "post-mortem". Note the thick lips which form a V-shape outline and the recess beneath it.

Fig. 1

Fig. 2

Fig. 1

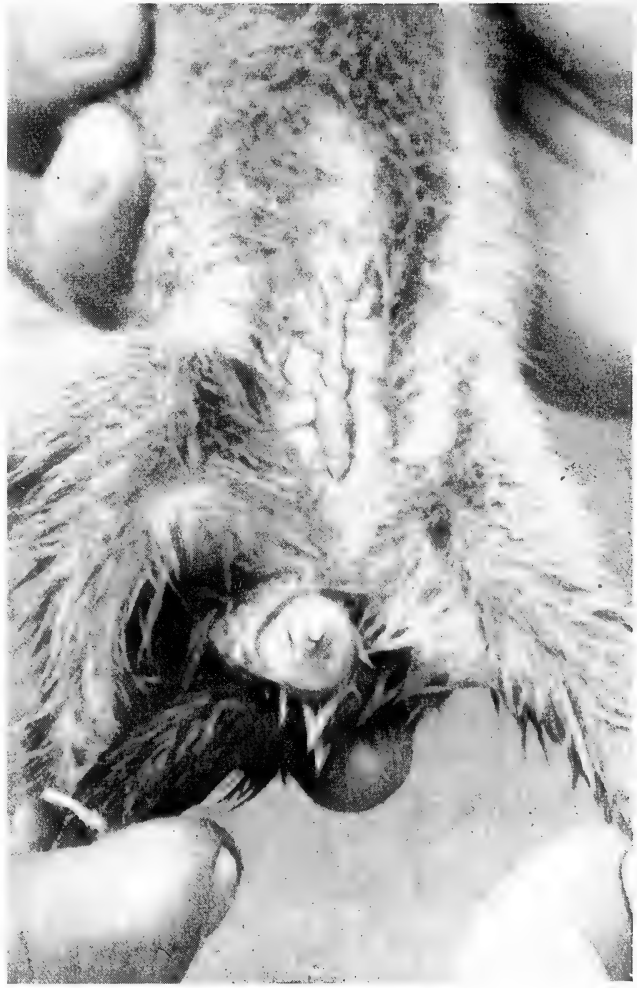

Fig. 2

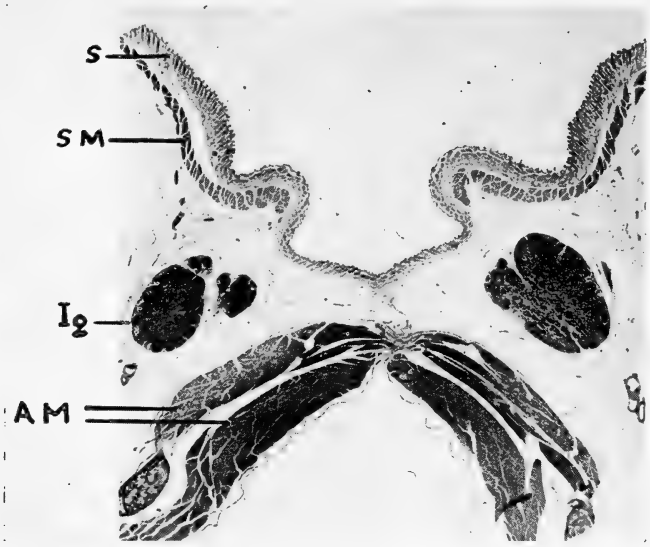

Fig. 1

Fig. 2

Plate XVII.

Fig. 1 (Experiment Y218).—Experimentally produced pouch-like indentation in a male of about $5\frac{1}{2}$ months of age. Photograph was taken "post-mortem" from the specimen hardened in formalin. Note the parallel lips and the lateral infolding which, however, is absent at the caudal end of the "pouch". This imperfection and the comparative shortness of the pouch may have been due to the fact that a too large part of the scrotum had been amputated at the beginning of the experiment.

Fig. 2 (Experiment Y211).—Photograph of a living male phalanger of five months of age. Note the close apposition of the thickened and puckered lips of the experimentally produced "pouch".

The appearance of a normal scrotum of *Trichosurus vulpecula* of approximately three months of age is depicted in a previous communication (Bolliger and Carrodus, 1940*c*).

Plate XVIII.

Fig. 1 (Experiment Y218).—Transverse section of the lower abdominal wall where the experimentally produced pouch is situated. Section shows the insinking and infolding of the skin, the thickened skin muscle, the broad layer of subcutaneous tissue and the enlarged inguinal glands. Magnification $\times 5$ approximately.

The second and more lateral fold in the abdominal skin above the inguinal glands is an artefact which formed in the process of embedding.

S.=skin, SM.=skin muscle, Ig.=inguinal gland, AM.=abdominal muscle.

Fig. 2.—Greatly enlarged mammary gland which brought on prolapse of the pouch. The neck of this "scrotum-like" structure is not easily seen in this picture because the struggling animal endeavoured to retract the gland.

CO-ORDINATION COMPOUNDS DERIVED FROM NICOTINYLACETONE.

By Francis Lions, B.Sc., Ph.D.,
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and Ernest Ritchie, M.Sc.

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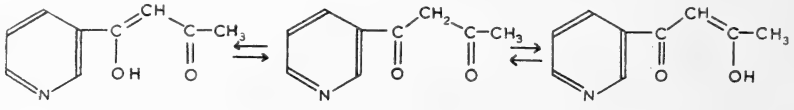
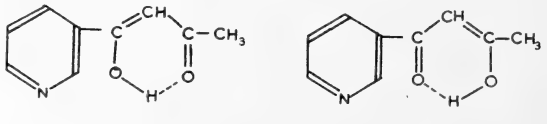
Among the more interesting applications of the 1 : 3-diketones to the stereochemistry of the metals was the preparation by Mills and Gotts (1926) of the copper, beryllium and zinc derivatives of benzoyl-pyruvic acid, and the demonstration that the brucine salt of the beryllium complex exhibited very definite mutarotation—considered to be possible only if the two β-diketone residues were tetrahedrally disposed about the central beryllium atom. Some claim was also advanced that the disposition of the metal valencies in the copper derivative was also tetrahedral, but the supporting evidence was not so conclusive.

It occurred to the authors that an extension of Mills and Gotts's experiments might be made using a β-diketone which contained, as salt-forming group, a basic group instead of the adjacent acid carboxyl group of benzoyl pyruvic acid. In the first place, there may be some possibility of the carboxyl group taking part in the co-ordination process when benzoyl pyruvic acid is used ; and, secondly, the inclusion of a basic group in the β-diketone molecule would enable the employment of the powerful camphor acids in endeavours to obtain resolution of the metal complexes. Hence, it was decided to study some of the co-ordination compounds derivable from nicotinylacetone (I), an unsymmetrical β-diketone described by Kuick and Adkins (1935).



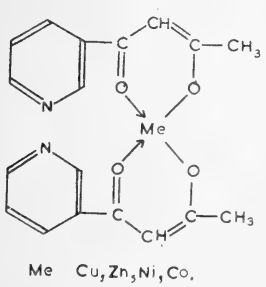
II I III

Because of its unsymmetrical character, both the enolic forms II and III should be derivable from nicotinylacetone ; and Kuick and Adkins, from alcoholysis and hydrogenolysis experiments, concluded that both enolic forms exist, and that the equilibrium between the two forms is in favour of III. However, it should be remembered that Sidgwick (1925) concluded, from a review of the chemical evidence, that the enolic forms of β-diketones exist as cyclic structures in which the hydrogen is " bonded " to the carbonyl oxygen atoms, as shown in IV and V—a view confirmed to some extent by the fact that the characteristic –OH group absorption in the infra-red is missing in β-diketones.

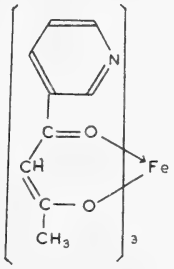


IV V

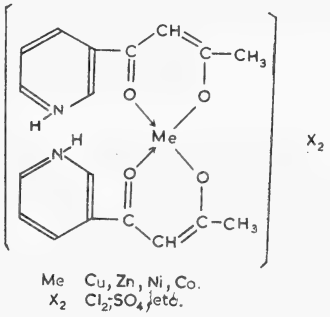
Nicotinylacetone was found to react readily with metal hydroxides, such as those of copper, zinc, nickel and cobalt, to give co-ordination compounds of the type VI—insoluble substances which char without melting when heated. On the other hand, ferric hydroxide was readily dissolved by excess nicotinylacetone to give a deep red complex, VII, containing three nicotinylacetone residues to each iron atom, not melting below 300°, and readily soluble in water, alcohol, benzene and acetone.



VI

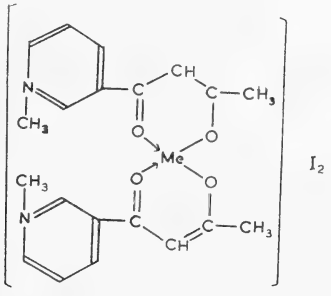


VII



VIII

These same complexes (VI) could also be obtained in other ways—e.g. (*a*) by the action of sodio-nicotinylacetone solutions on solutions of the appropriate metal salts; or (*b*) by the action of sodium hydroxide on the appropriate metallic salt complexes VIII described below. It is important to note that the pyridine nuclei of the nicotinylacetone residues in these complexes VI are not concerned in the co-ordination process, and, consequently, retain their basic properties. The complexes VI can, therefore, be combined with acids to give salts of the type VIII. They can also react with methyliodide to give metho salts of the type IX.

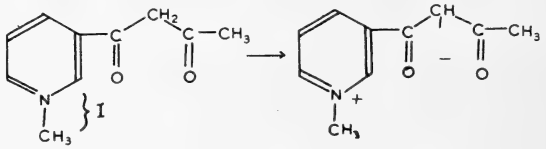


IX

The salts VIII are also conveniently prepared by the direct union of nicotinylacetone with the appropriate metallic salts; whilst the metho salts, IX, can also be obtained from metallic hydroxides and the methiodide of nicotinylacetone (X), a crystalline substance readily prepared from the diketone by heating with excess methyliodide in a closed tube at 100°. This methiodide (X) could be converted in absolute alcoholic solution by sodium ethoxide to the pale brown, extremely water-soluble betaine XI.

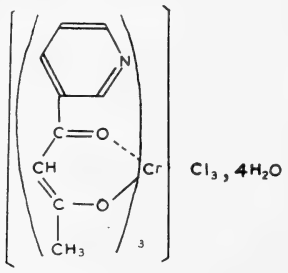
The salts of type VIII were found to be soluble usually in water or hydroxylic solvents, and behaved as typical electrolytes containing a complex cation.

Silver chloride and barium sulphate could be quantitatively precipitated by addition of silver nitrate or barium chloride solutions to the aqueous solutions of the respective chlorides or sulphates (VIII).



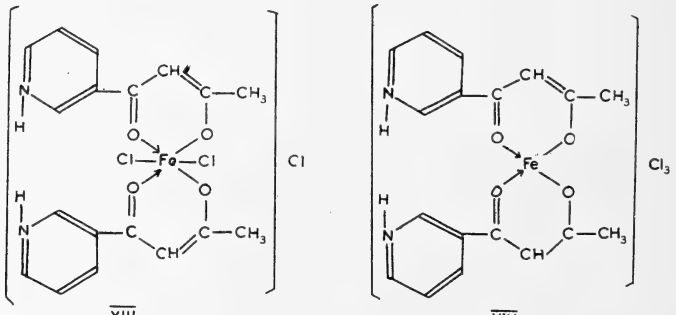
X XI

Nicotinylacetone reacted apparently normally with chromic chloride in acetone solution to give the complex XII ; but with ferric chloride a substance



XII

was obtained whose structure is, apparently, not so simple. Analysis showed it to possess the formula $C_{18}H_{18}O_4N_2FeCl_3$—indicating the combination of one ferric chloride molecule with two nicotinylacetone molecules. Such a substance should have molecular weight 488·5. However, cryoscopic determinations with water as solvent showed the molecular weight to be of the order of 128–130—about one-quarter of the expected value. These results suggest a dissociation of the complex in aqueous solution into four ions. Measurements of conductivity also supported this view. On the other hand, the behaviour of dilute aqueous solutions of the complex with silver nitrate leads to the conclusion that at least two of the chlorine atoms are covalently held in the molecule, only a slight precipitation of silver chloride occurring. The precipitation was increased on heating, but the chlorine could not be completely precipitated until after the addition of nitric acid. A formula such as XIII would express this non-ionic



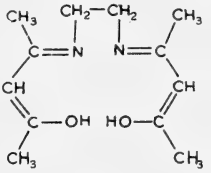
XIII XIV

state of two-thirds of the chlorine present in the complex, but fails to account for the dissociation of the complex in dilute solution into four ions. A formula such as XIV, in which the iron is considered to be 4-covalent, would account for the dissociation of the complex into four ions, but would not account for the

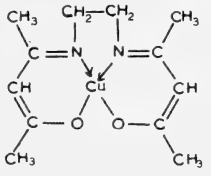
non-ionic behaviour of the chlorine ; and, further, would not account adequately for the ready formation of the complex from ferric nicotinylacetone (VII) by action of hydrochloric acid.

In attempts to prepare salts of the type VIII in which the acid radical was optically active, cupric α-bromo camphor-π-sulphonate, and the corresponding zinc salt were prepared and combined in correct proportions with nicotinylacetone but only gummy materials, which could not be crystallised, were obtained. Resolution experiments with them could not, therefore, be attempted.

Morgan and Main Smith (1926) established that the condensation product of ethylene diamine with acetyl acetone (ethylene diamine bis acetylacetone (XV)) could function as a quadridentate group, the violet copper salt of which (XVI) had been described by Combes (1889). It seemed, therefore, to be of interest

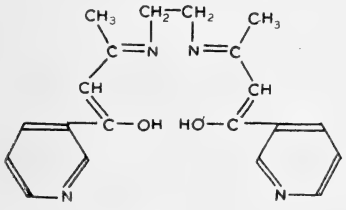


XV

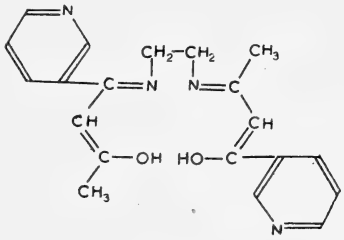


XVI

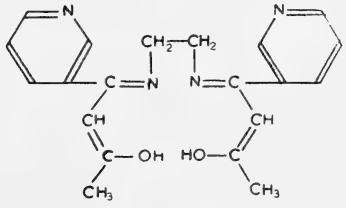
to study the behaviour of the condensation product of ethylene diamine and nicotinylacetone with suitable metallic hydroxides and metallic salts. Since nicotinylacetone is an unsymmetrical diketone it might be expected that condensation of ethylene diamine with nicotinylacetone would lead to the three ethylene diamine bis nicotinylacetones (XVII), (XVIII) and (XIX). However,



XVII



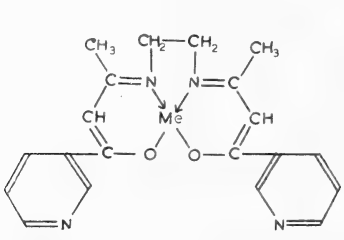
XVIII



XIX

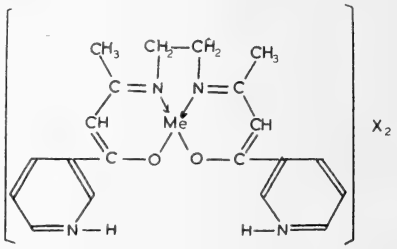
experiment shows that ethylene diamine condenses readily with nicotinylacetone to give one substance only in practically quantitative yield, and there can be little doubt from the work of Kuick and Adkins (*loc. cit.*) that this has the formula XVII. This substance behaves as a quadridentate group, co-ordinating through two primary valencies and two secondary valencies. It reacts with metallic acetates, such as copper acetate, nickel acetate and zinc acetate to form metallic complexes of the type XX. Of these, the nickel and copper complexes each contain one molecule of water, behave as non-electrolytes, are

soluble in organic solvents, and have definite melting points. The nickel complex may even be boiled out of contact with air, only slight decomposition occurring. The complexes are stable to ethylene diamine and may be recrystallised unchanged from solutions in ethylene diamine monohydrate. Morgan and Main Smith postulated a coordination valency of five for copper in the green monohydrate corresponding to the violet anhydrous copper compound XVI, but in view of the similarity between the abovementioned copper and nickel complexes, and the fact that a coordination valency of five is very unlikely for nickel it seems more reasonable to assume that in them both nickel and copper exhibit coordination valencies of four, and that the molecule of water is necessary for the building of the crystal lattice or is held by hydrogen bonds to one or other of the two oxygen atoms of the complex. The zinc complex is anhydrous, and in it zinc appears to have its normal covalency of four.



XX

Me = Cu, Ni, Zn.



XXI

Me = Cu, Ni, Zn.
X = Cl, etc.

The complexes XX each contain two pyridine nuclei, the nitrogen atoms of which take no part in the formation of the central co-ordination complex. They are therefore capable of union with acids to form salts of the type XXI. These salts may also be directly obtained from ethylene—diamine bis-nicotinylacetone itself and metallic salts such as the chlorides of copper, nickel, zinc, cobalt, etc., and come down in anhydrous condition by precipitation from alcoholic solution. They are all soluble to some extent in hydroxylic solvents, but insoluble in anhydrous organic solvents.

Experimental.

Nicotinylacetone (*I*) was prepared by a method substantially similar to that developed by Kuick and Adkins (*loc. cit.*). It readily formed a yellow *picrate*, which was obtained in yellow needles melting at 155°.

Found : C, 45·8, H, 3·3% ; calculated for $C_{15}H_{12}O_9N_4$, C, 45·9, H, 3·1%.

Nicotinylacetone Methiodide (*X*). Nicotinylacetone (16 g.) and methyl iodide (30 g. ; excess) were heated together in a closed tube at 100° for 30 minutes. The first-formed homogeneous yellow solution soon deposited a mass of yellow crystals. Recrystallised from alcohol or water the substance was obtained in yellow prisms melting at 184°.

Found : C, 39·0, H, 4·0, I, 41·6% ; calculated for $C_{10}H_{12}O_2NI$, C, 39·4, H, 3·9, I, 41·6%.

This metho salt is very soluble in water, and soluble in alcohol, but is insoluble in anhydrous organic solvents. When its solution in absolute alcohol was treated with the theoretical amount of sodium ethoxide in dry alcoholic solution a light yellow precipitate, which soon turned brown, was formed. When collected, washed with absolute alcohol and dried *in vacuo* a brown powder, extremely soluble in water and aqueous alcohol, but insoluble in absolute alcohol was obtained. It was difficult to obtain it free from traces of sodium iodide, but analysis indicated strongly that it was the *betaine* IX.

Found : C, 66·4, H, 6·2% ; calculated for $C_{10}H_{11}O_2N$, C, 67·9, H, 6·8%.

Ethylenediamine bis-Nicotinylacetone (*XVII*). (β : β′-*Ethylenediamino bis* (*propenyl-3-pyridyl ketone*). Nicotinylacetone (16·3 g. ; 2 mols.) was mixed with ethylenediamine monohydrate (3·9 g. ; 1 mol.) in a large test-tube, and the mixture gently warmed. Water was separated in the moderately vigorous reaction which set in. The mixture was finally heated at 100° for an hour. After cooling the crystalline yellow mass was recrystallised from benzene and thus obtained in yellow prisms melting at 170°. The yield was almost theoretical. The substance was readily soluble in water, alcohol, benzene and chloroform.

Found : C, 68·0, H, 6·3, N, 15·8% ; calculated for $C_{20}H_{22}O_2N_4$, C, 68·6, H, 6·3, N, 16·0%.

The methods employed for preparation of the metallic complexes VI and the salts VIII were quite similar in experimental details, which are described in full for the preparation of the copper and zinc derivatives, whilst only a brief description of the complexes containing nickel and cobalt is given.

Cupric Nicotinylacetonate (*VI ; Me=Cu*). (*a*) The well washed cupric hydroxide from copper sulphate (2·4 g.) and potassium hydroxide solution (40 ml. of 0·5 N) was suspended in an alcoholic solution of nicotinylacetone (3 g.) and digested for several days. The gelatinous hydroxide was gradually converted into an insoluble green powder which was well washed with water and alcohol, and dried *in vacuo* over sulphuric acid.

(*b*) A purer sample was prepared by mixing an aqueous solution of copper sulphate (2·4 g.) and an aqueous alcoholic solution containing nicotinylacetone (3 g.) and potassium hydroxide solution (40 ml. of 0·5 N). The precipitated metallic complex formed green micro crystals insoluble in water or organic solvents, readily decomposed by excess of mineral acids, and charring above 320° without melting.

Found : Cu, 16·4, C, 55·7, H, 4·2% ; calculated for $C_{18}H_{16}O_4N_2Cu$, Cu, 16·4, C, 55·8, H, 4·1%.

Treatment of this complex (1 g.) with sulphuric acid (0·25 g.) led to formation of the complex bis nicotinyl acetone cupric sulphate (Cu, 13·3%) described below ; whilst treatment of it (1 g.) with hydrochloric acid (0·18 g.) led to formation of the complex bis nicotinyl acetone cupric chloride (Cu, 14·1%, m.p. 189°) described below.

Bis Nicotinyl Acetone Cupric Chloride (*VIII ; Me=Cu, X=Cl*). To a solution of nicotinyl acetone (1·6 g. ; 2 mols.) in a little alcohol was added an alcoholic solution of cupric chloride (0·85 g. ; 1 mol.). A green powder was obtained, practically insoluble in most of the solvents tried, but slightly soluble in dioxane. Recrystallised from this latter solvent it was obtained as a fine green crystalline powder melting at 190°.

Found : Cu, 13·7, C, 46·6, H, 3·9% ; calculated for $C_{18}H_{18}O_4N_2CuCl_2$, Cu, 13·8, C, 46·9, H, 3·9%.

Bis Nicotinyl Acetone Cupric Sulphate (*VIII ; Me=Cu, $-X_2$ $=SO_4$*). A concentrated solution of cupric sulphate (2·4 g. ; 1 mol.) in hot water was added to a solution of nicotinylacetone (3 g. ; 2 mols.) in alcohol. A thick green precipitate was formed. It was collected and dried. It appeared to be insoluble in alcohol and organic solvents but was moderately soluble in water. Recrystallised from this solvent it was obtained in fine green needles which charred at about 280°.

Found : Cu, 13·0, C, 44·0, H, 3·7, SO_4, 19·4% ; calculated for $C_{18}H_{18}O_4N_2CuSO_4$, Cu, 13·1, C, 44·4, H, 3·7, SO_4, 19·8%.

Addition of a solution of sodium hydroxide (0·08 g. ; 2 mols.) to an aqueous solution of this complex sulphate led to formation of a green precipitate of the cupric nicotinyl acetonate (found : C, 55·4, H, 4·2%) described above.

Cupric bis Nicotinyl Acetone α Bromocamphor-π-Sulphonate. An alcoholic solution of nicotinyl acetone (3·6 g. ; 2 mols.) was added to a moderately concentrated aqueous solution of cupric α-bromocamphor-π-sulphonate (9 g. ; 1 mol.). The resulting green solution was then evaporated to dryness *in vacuo*, leaving a green gum which, on prolonged drying, was converted into a green glass. This was found to be soluble in alcohol, acetone, chloroform and water, but was insoluble in benzine and ether. All attempts to crystallise the substance failed. Analysis of portion of the glass gave Cu, 6·03% ; the calculated value for anhydrous $C_{38}H_{46}O_{12}Br_2N_2S_2Cu$ is Cu, 6·3%.

Zinc Nicotinyl Acetonate (*VI*; *Me*=*Zn*). (*a*) Well-washed zinc hydroxide (from zinc nitrate (3 g.) and 0·5 N potassium hydroxide solution (40 ml.) was digested for some days with an alcoholic solution of nicotinylacetone (3 g.) in alcohol. The gelatinous hydroxide was slowly converted to a yellow, micro-crystalline powder (containing 17·3% of zinc).

(*b*) A solution of zinc nitrate (3 g.) in aqueous alcohol was added to an aqueous alcoholic solution containing nicotinyl acetone (3 g.) and 0·5 N alkali solution (40 ml.). The yellow powder which precipitated was washed and dried.

(*c*) Addition of the correct quantity of sodium hydroxide solution to an aqueous solution of bis nicotinyl acetone zinc chloride (described below) gave a yellow precipitate of zinc nicotinyl acetonate.

This zinc complex is a yellow insoluble powder which chars without melting above 300°.

Found: Zn, 16·6, C, 55·2, H, 4·2%; calculated for $C_{18}H_{16}O_4N_2Zn$, Zn, 16·8, C, 55·5, H, 4·1%.

This complex (0·4 g.; 1 mol.) dissolved readily in dilute hydrochloric acid (0·073 g. HCl; 2 mols.) to a yellow solution, which, on evaporation, yielded yellow crystals melting at 140° of bis nicotinyl acetone zinc chloride (described below).

Bis Nicotinyl Acetone Zinc Chloride (*VIII*; *Me*=*Zn*, *X*=*Cl*). Alcoholic solutions of zinc chloride (1·4 g.) and nicotinylacetone (3 g.) were mixed, and then reduced to small bulk, when yellow needles separated. After recrystallisation from alcohol they melted at 140°. They were slightly soluble in water.

Found: Zn, 13·9, C, 46·3, H, 3·9, Cl, 15·1%; calculated for $C_{18}H_{18}O_4N_2ZnCl_2$, Zn, 14·1, C, 46·7, H, 3·9, Cl, 15·3%.

Treatment of an aqueous solution of this salt (0·5 g.) with a solution of sodium hydroxide (0·08 g.) gave a yellow insoluble precipitate of the zinc nicotinyl acetonate (Zn, 16·6%) described above.

Bis Nicotinyl Acetone Zinc Sulphate (*VIII*; *Me*=*Zn*, X_2=SO_4). This substance was obtained as a yellow insoluble powder, infusible below 300° by mixing solutions of zinc sulphate (1·4 g.) and nicotinylacetone (3 g.).

Found: Zn, 13·1, C, 44·0, H, 3·7%; calculated for $C_{18}H_{18}O_8N_2ZnS$, Zn, 13·4, C, 44·3, H, 3·7%.

Zinc bis-Nicotinylacetonate-α-Bromocamphor-π-Sulphonate. Alcoholic solutions of zinc α-bromocamphor-π-sulphonate (30 g.; 1 mol.) and nicotinylacetone (11·8 g.; 2 mols.) were mixed, and the solution then cautiously evaporated *in vacuo*. A clear yellow glass was left. It was found to be extremely soluble in water and in alcohol but insoluble in organic solvents. Additions of dry ether to its alcoholic solution effected its precipitation as a slightly gummy mass, which was dried *in vacuo* to a yellow powder.

Found: Zn, 6·44%; calculated for $C_{38}H_{46}O_{12}Br_2N_2S_2Zn$, Zn, 6·47%.

Many attempts were made to recrystallise this substance but all resulted only in the formation of yellow gums.

Nickel bis Nicotinylacetonate (*VI*; *Me*=*Ni*). Prepared by the usual methods this substance formed a green micro-crystalline insoluble powder which charred above 300° without melting.

Found: Ni, 15·6, C, 55·9, H, 4·1%; calculated for $C_{18}H_{16}O_4N_2Ni$: Ni, 15·4, C, 56·4 H, 4·2%.

Bis-Nicotinylacetone Nickel Chloride (*VIII*; *Me*=*Ni*, *X*=*Cl*). Prepared by mixing alcoholic solutions of nickel chloride (2·4 g.) and nicotinylacetone (3·2 g.) and then recrystallisation from aqueous alcohol, this substance was obtained in fine green needles slightly soluble in alcohol and water, but insoluble in solvents such as benzene. Above 300° it chars without melting.

Found: Ni, 13·1, C, 45·9, H, 3·9%; calculated for $C_{18}H_{18}O_4N_2NiCl_2$: Ni, 12·9, C, 47·3, H, 4·0%.

Bis-Nicotinylacetone Nickel Sulphate (*VIII*; *Me*=*Ni*, X_2=SO_4). This substance, prepared in the usual way, was a greenish yellow powder, which charred on heating without melting. It was very insoluble in all the usual solvents.

Found: Ni, 11·9, C, 45·6, H, 3·8%; calculated for $C_{18}H_{18}O_4N_2 . NiSO_4$: Ni, 12·2, C, 44·9, H, 3·8%.

Cobaltous bis Nicotinylacetonate (*VI*; *Me=Co*). Prepared by the usual methods, this substance formed a yellow powder, insoluble in water and organic solvents, and charring when heated.

Found: Co, 15·3, C, 54·9, H, 4·2%; calculated for $C_{18}H_{16}O_4N_2Co$: Co, 15·4, C, 56·4, H, 4·2%.

Bis-Nicotinylacetone Cobaltous Chloride (*IX*; *Me=Co, X=Cl*). This substance was obtained crystalline as a brown solid after recrystallisation from alcohol. It is readily soluble in alcohol and in water.

Found: Co, 12·6, C, 46·6, H, 4·0%; calculated for $C_{18}H_{18}O_4N_2Cl_2Co$: Co, 12·9, C, 47·3, H, 4·0%.

Bis-Nicotinylacetone Silver Nitrate. Hot aqueous alcoholic solutions of silver nitrate (3·4 g.; 1 mol.) and nicotinylacetone (6·5 g.; 2 mols.) were mixed. On cooling, white acicular crystals separated. They were collected, washed, and dried. They then melted at 121°, and were found to be soluble in alcohol, chloroform acetone, ethylacetate, but only slightly soluble in water and insoluble in benzene and toluene.

Addition of a chloride to an aqueous alcoholic solution of the complex led to an immediate precipitation of silver chloride.

Found: Ag, 22·5, C, 45·4, H, 3·8%; calculated for $C_{18}H_{18}O_5N_3Ag$: Ag, 22·4, C, 44·2, H, 3·9%.

Addition of potassium hydroxide (1 mol.) in aqueous solution to this complex (1 mol.) gave a black tarry precipitate containing metallic silver—formed probably owing to the formation and subsequent decomposition of silver nicotinylacetonate—a behaviour similar to that of silver acetylacetonate (cf. Morgan and Moss, 1914).

Ferric Nicotinylacetonate (*VII*). Freshly precipitated ferric hydroxide from ferric alum (5 g.; 1 mol.) was well washed with water and alcohol, and then dissolved in an alcoholic solution of nicotinylacetone (4·5 g.; 3 mols.). The deep red solution so formed was evaporated to dryness and the red solid residue well washed with ether, then dried. The substance was eventually obtained in red scales not fusible below 300°, and extremely soluble in water, acetone, alcohol and benzene.

Found: Fe, 10·6, C, 59·3, H, 4·4%; calculated for $C_{27}H_{24}O_6N_3Fe$: Fe, 10·5, C, 59·8, H, 4·4%.

Bis Nicotinylacetone Ferric Chloride. A solution of nicotinylacetone (4·9%; 3 mols.) in aqueous alcohol was added to a solution of anhydrous ferric chloride (1·6 g.; 1 mol.) in aqueous alcohol (25 ml.). The solution was then evaporated to about 50 ml. on the water-bath and allowed to cool. The small dark red crystals which separated were collected. They were found to be very soluble in water but insoluble in absolute alcohol and anhydrous solvents. They did not melt below 300°.

Found: Fe, 11·1, C, 43·3, H, 3·8, Cl, 21·4%; calculated for $C_{18}H_{18}O_4N_2Cl_3Fe$: Fe, 11·4, C, 44·2, H, 3·7, Cl, 21·8%.

Excess caustic soda solution precipitates ferric hydroxide from aqueous solutions of this complex, but silver nitrate solution in the cold gives only a small precipitate of silver chloride.

The complex can also be obtained from ferric nicotinylacetonate by treating it (1·1 g.; 1 mol.) with N/2 hydrochloric acid (12 ml.; 3 mols.).

Tris-Nicotinylacetone Chromic Chloride (*XII*). Anhydrous chromic chloride (1·6 g.; 1 mol.) was dissolved in acetone by refluxing in presence of a small amount of metallic chromium. An acetone solution of nicotinylacetone (3·2 g.) was then added, and the resulting green solution evaporated to small bulk when fine green needles separated. After recrystallisation from alcohol, these melted at 105° to a green liquid.

Found: Cr, 7·4, C, 45·2, H, 4·7%; calculated for $C_{27}H_{27}O_6N_3Cl_3Cr \cdot 4H_2O$: Cr, 7·24, C, 45·1, H, 4·8%.

Cupric bis Nicotinylacetonate Methiodide (*IX*; *Me=Cu*). (*a*) Well washed cupric hydroxide from cupric nitrate (1·5 g.) was digested on a water-bath with an aqueous alcoholic solution of nicotinylacetone methiodide (3 g.; 2 mols.). It gradually dissolved, forming a green solution from which the complex crystallised on cooling.

(*b*) Cupric bis nicotinylacetonate was heated in a sealed tube at 100° with an excess of methyl iodide. After removal of the excess the product was recrystallised from aqueous alcohol. It forms fine yellowish green needles, soluble in water and alcohol, but insoluble in organic solvents. When heated, it darkens above 100° and melts at 188°.

Found : Cu, 8·7, C, 32·5, H, 4·1% ; calculated for $C_{20}H_{22}O_4N_2I_2Cu \cdot 4H_2O$: Cu, 8·6, C, 32·4, H, 4·0%.

Zinc bis Nicotinylacetonate Methiodide (*IX ; Me=Zn*). Prepared by methods exactly similar to those described for the copper salt, this derivative was obtained in short yellow needles, melting at 146°, when recrystallised from aqueous alcohol.

Found : Zn, 8·4, C, 30·6, H, 3·9, I, 32·6% ; calculated for $C_{20}H_{22}O_4N_2I_2Zn \cdot 6H_2O$: Zn, 8·4, C, 30·7, H, 4·4, I, 32·6%.

Beryllium bis Nicotinylacetonate Methiodide (*IX ; Me=Be*). An aqueous solution of beryllium sulphate (1·4 g. ; 1 mol.) was treated with 0·5 N sodium hydroxide solution (30 ml.) and the white flocculent precipitate collected, thoroughly washed, and then dissolved in an alcoholic solution of nicotinylacetone methiodide (4·5 g. ; 2 mols.) to a yellow solution. Concentration of this to about 30 ml. and cooling led to a crystallisation of fine yellow needles of the complex. After recrystallisation from aqueous alcohol these melted at 214°. They were soluble in water and alcohol, but insoluble in other organic solvents.

Found : Be, 1·37, C, 39·0, H, 3·6, I, 41·5% ; calculated for $C_{20}H_{22}O_4N_2BeI_2$: Be, 1·46, C, 38·9, H, 3·6, I, 41·2%.

Cupric Ethylenediamine bis-Nicotinylacetonate (*XX ; Me=Cu*). A solution of cupric acetate (2 g. ; 1 mol.) in the minimum quantity of hot aqueous alcohol was added to a boiling alcoholic solution of ethylenediamine bis nicotinylacetone. A deep purplish green solution resulted from which brown crystals were deposited on cooling. Recrystallised from alcohol, these came out as long hair-like crystals, melting at 167°, and readily soluble in alcohol, acetone, benzene and chloroform.

Found : Cu, 14·4, C, 55·6, H, 5·2% ; calculated for $C_{20}H_{20}O_2N_4Cu \cdot H_2O$: Cu, 14·2, C, 56·0, H, 5·2%.

Zinc Ethylenediamine bis-Nicotinylacetonate (*XX ; Me=Zn*). This derivative was prepared in a manner exactly similar to that described for the copper derivative. It formed fine yellow crystals insoluble in water and only slightly soluble in alcohol and chloroform. It melted at 228°.

Found : Zn, 15·3, C, 58·2, H, 4·5% ; calculated for $C_{20}H_{20}O_2N_4Zn$: Zn, 15·8, C, 58·0, H, 4·8%.

Nickel Ethylenediamine bis-Nicotinylacetonate (*XX ; Me=Ni*). Obtained from nickel acetate and ethylenediamine bis-nicotinylacetone in alcoholic solution, as described for the copper derivative, this substance crystallised from alcohol in red needles melting at 258°. It dissolved in alcohol, benzene and chloroform giving a red solution in each instance. It was also very slightly soluble in water.

Found : Ni, 13·4, C, 56·7, H, 5·1% ; calculated for $C_{20}H_{20}O_2N_4Ni \cdot H_2O$: Ni, 13·8, C, 56·7, H, 5·2%.

Cobalt Ethylenediamine bis-Nicotinylacetonate (*XX ; Me=Co*). Prepared in the manner described above from cobalt acetate and ethylenediamine bis nicotinylacetone, and recrystallised from alcohol, this substance formed dark red crystals melting at 165°.

Found : Co, 10·6, C, 47·3, H, 6·3% ; calculated for $C_{20}H_{20}O_2N_4Co \cdot 6H_2O$: Co, 11·4, C, 46·6, H, 6·2%.

Cupric Ethylenediamine bis-Nicotinylacetonate Dihydrochloride (*XXI ; Me=Cu*). A solution of cupric chloride (0·9 g. ; 1 mol.) in hot absolute alcohol was added to a solution of ethylenediamine bis-nicotinylacetone (1·8 g. ; 1 mol.) in absolute alcohol. A light green powder precipitated. It was collected and crystallised from aqueous alcohol and thus obtained in fine green needles, melting to a dark brown liquid at 200°, and soluble in water and aqueous alcohol.

Found : Cu, 12·8, C, 50·3, H, 4·6% ; calculated for $C_{20}H_{22}O_2N_4CuCl_2$: Cu, 13·1, C, 49·6, H, 4·5%.

Zinc Ethylenediamine bis-Nicotinylacetonate Dihydrochloride (*XXI; Me=Zn*). Prepared as described for the copper derivative, this substance came down first as a yellow gum, which solidified on cooling. It was slightly soluble in alcohol and in water, and melted at 253°.

Found: Zn, 13·0, C, 48·8, H, 4·6, Cl, 14·4%; calculated for $C_{20}H_{22}O_2N_4ZnCl_2$: Zn, 13·4, C, 49·4, H, 4·5, Cl, 14·6%.

Nickel Ethylenediamine bis-Nicotinylacetonate Dihydrochloride (*XXI; Me=Ni*). Prepared by the method described above from nickel chloride and ethylene diamine bis nicotinylacetone in alcoholic solution, this substance was obtained in fine green needles which darkened on heating at 200° and melted at 276°. The substance dissolved in water to a yellow solution but was insoluble in organic solvents.

Found: Ni, 12·0, C, 49·3, H, 4·6%; calculated for $C_{20}H_{22}O_2N_4NiCl_2$: Ni, 12·3, C, 50·0, H, 4·6%.

Cobalt Ethylenediamine bis-Nicotinylacetonate Dihydrochloride (*XXI; Me=Co*). Prepared by a method similar to that described above, and recrystallised from aqueous alcohol, this substance formed blue crystals which dissolved in water, or aqueous alcohol, to red solutions. The crystals melted at 242° with decomposition.

Found: Co, 12·7, C, 49·4, H, 4·7%; calculated for $C_{20}H_{22}O_2N_4CoCl_2$: Co, 12·3, C, 50·0, H, 4·6%.

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References.

Combes, 1889. *C.R. Acad. Sci.*, **108**, 1252.
Kuick and Adams, 1935. *J. Amer. Chem. Soc.*, **57**, 143.
Mills and Gotts, 1926. *J. Chem. Soc.*, 3121.
Morgan and Moss, 1914. *J. Chem. Soc.*, **105**, 189.
Morgan and Main-Smith, 1926. *J. Chem. Soc.*, **129**, 912.
Sidgwick, 1925. *J. Chem. Soc.*, **127**, 907.

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PROGRESSIVE RATES OF TAX IN AUSTRALIA. II.

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Introductory.

In a paper with the same title, read to this Society on May 7, 1941, I discussed the rates of the Federal income tax on individual incomes from its introduction in 1915 to that of the Income Tax Act (No. 2), 1940, which dealt with income received in the year ending June 30, 1940. A discussion of the different State income tax rates for the last-named year was also given.

In view of the important changes that have taken place since that paper was read, I propose in this supplement to bring the discussion up to date. On this occasion nothing need be said about the State taxes.

The War-time Loan Contribution Proposal.

1. Early in 1941, Mr. Fadden, still Treasurer in the second Menzies Government, attempted without success to come to some arrangement with the State Governments which would ensure greater uniformity in taxation of incomes. In August of that year he succeeded Mr. Menzies as Prime Minister but retained the portfolio of the Treasury. On September 25th he introduced the budget for 1941–42. His financial proposals included increased revenue from taxation, directly or indirectly, on incomes, in the following way :

A new Federal income tax scale was proposed with much the same tax as the last one except on incomes over about £3,000. On earned income the excess over £3,350 and on property income the excess over £2,750 were to be taxed at a flat rate of 11s. 3d. in the £ ; but in arriving at the taxable income for Federal purposes the State income tax paid in the previous year would no longer be an allowable deduction.

A " National Contribution " was to be assessed on every income in Australia and in this no discrimination was to be made between earned and property income. The exemption for a person without dependants was to be £100 and the scale of contribution was to rise so that on the excess over £3,900 there would be a flat rate of 18s. 6d. in the £. The National Contribution would in general be large enough to cover both Federal income tax and State income tax in the highest taxing State, both on the property scale. If it were found that this aim had not been achieved, it was hoped that the State tax on high incomes might be reduced accordingly.

From the assessed National Contribution on any income the Federal income tax paid in the current year and the State income tax paid in the previous year were to be deducted. The remainder, if any, was to be collected as a loan, bearing interest at the rate of 2 per cent., and repayable after the war. This remainder was the " War-time Loan Contribution " and came to be called a " Post-War Credit ". If the sum of the Federal income tax and the State income tax paid in the previous year was greater than the assessed National Contribution on that income, there would be no Post-War Credit.

By this device, except in the lastmentioned case, the sum of the Federal Income tax, the State income tax and the Post-War Credit on any income would be the same, no matter in what State the taxpayers with that income resided.

The details of the scales to be adopted for 1941–42 for the National Contribution and the Federal income tax for individuals as well as companies were to be given in Bills to be introduced later, but tables were issued to Members of Parliament and communicated to the Press, which showed what the burden would be on individual incomes over a wide range. It will be sufficient here to give the table containing the proposed Federal income tax, National Contribution and Post-War Credit of a person without dependants whose income is derived from personal exertion. As remarked above, the National Contribution of a taxpayer was not to depend on the nature, earned or property, of his income.

Income from Personal Exertion.
Proposed Federal Taxes and National Loan Contributions 1941–42.
Person with no Dependants.
24th September, 1941.

Actual Income.[1]	National Contribution.[2]	Federal Income Tax.	State Taxes, 1940–41.		Loan. (Post-War Credit.)	
			Highest Taxing State.	Lowest Taxing State.	Highest Taxing State.	Lowest Taxing State.
£	£	£	£	£	£	£
100	—	—	0·6	—	—	—
150	11·1	—	7·0	—	4·1	11·1
200	22·2	—	11·7	1·3	10·5	20·9
250	33·3	6·3	17·5	4·3	9·5	22·7
300	44·4	12·5	23·5	6·4	8·4	25·5
350	55·6	18·8	29·5	8·7	7·3	28·1
400	66·7	25·0	35·6	11·0	6·1	30·7
500	95·1	40·1	47·9	16·0	7·1	39·0
600	126·9	57·7	60·4	29·3	8·8	39·9
800	199·6	99·7	86·0	42·8	13·9	57·1
1,000	282·9	149·7	112·5	57·0	20·7	76·2
1,500	531·0	304·0	191·0	101·0	36·0	126·0
2,000	828·0	496·0	290·0	154·0	42·0	178·0
3,000	1,543·0	970·0	542·0	284·0	31·0	289·0
5,000	3,296·0	2,089·0	1,257·0	542·0	Nil	665·0
10,000	7,796·0	4,902·0	3,751·0	1,207·0	,,	1,687·0
20,000	16,796·0	10,527·0	7,807·0	2,431·0	,,	3,838·0
40,000	34,796·0	21,777·0	15,920·0	4,861·0	,,	8,158·0

[1] Actual income here means the income remaining after allowing all allowable deductions except the Statutory Exemption and concessional deductions for dependants. State income tax is not an allowable deduction.

[2] The National Contribution is the gross amount assessable from which is deductible the sum of the Federal and State taxes in order to obtain the actual amount of the Loan (Post-War Credit).

As these proposals brought persons without dependants on a wage of £2 a week into the contributing class, with a slightly higher starting point for persons with dependants, it is not surprising that for this as well as other reasons they were strongly opposed by the Labour Opposition and not viewed with very great enthusiasm by some members not belonging to the Labour Party. After some days had been given to the discussion of these and other matters involved in the budget, an amendment, moved by Mr. Curtin on October 3rd, which practically amounted to its rejection, was carried on the same day. The

resignation of the Fadden Government followed and the Labour Party took office on October 7th with Mr. Curtin as Prime Minister.

The Formula giving the Amount of the National Contribution on any Individual Income.

2. The National Contribution, both for individuals and companies, as proposed by Mr. Fadden, has now mainly historical interest,[1] but, from the point of view of the development of the progressive rates of tax in Australia it would be a pity if the National Contribution scale, as well as the scales for Federal income tax on individuals, were to remain hidden among the papers of the Treasury. Mr. Fadden has kindly allowed me to make these formulæ public. In case of misunderstanding, I add that I am in no way responsible for them. One may safely ascribe them to the Economic Adviser (Professor Giblin), who must have been pleased at having succeeded in inserting a square root in the schedules. This would soothe his regret that, as Acting Commonwealth Statistician in 1931, he was responsible for depriving the Australian taxpayer of the unique distinction of paying an income tax which had to be calculated by the Integral Calculus.

The National Contribution on an individual income is determined by what is called the *Contributory Income*. On an *actual income* (the term is defined in a footnote to the above table) which does not exceed £100, of a person without dependants, the contributory income is nil. If the actual income of such a person exceeds £100 and does not exceed £400, the contributory income is the actual income less £100 diminished by £1 for every £3 by which it exceeds £100. This deduction vanishes when the actual income is £400 and from that stage on the contributory income and actual income are the same.

Let the actual income of this individual be £x and the contributory income £C.

$$\left.\begin{array}{lll} \text{Then, when} & 0<x\leqslant 100, & C=0\,; \\ \text{when} & 100<x\leqslant 400, & C=\dfrac{4(x-100)}{3}\,; \\ \text{and, when} & 400<x, & C=x. \end{array}\right\}$$

The Bill proposed that:

If the contributory income (£C) does not exceed £400, the amount of the National Contribution shall be $40C$ pence.

If the contributory income exceeds £400 and does not exceed £3,900, the amount of the National Contribution shall be $C(2\cdot 4\sqrt{C}-8)$ pence.

If the contributory income exceeds £3,900:

(a) The amount of the National Contribution on the first £3,900 shall be $141\cdot 88\times 3{,}900$ pence; and

(b) every £ of the excess over £3,900 shall pay 216 pence.

Now let the National Contribution of a person without dependants whose actual income is £x be y pence.

From what has been said above, we see that

$$\left.\begin{array}{lll} \text{when} & 0<x\leqslant 100, & y=0\,; \\ \text{when} & 100<x\leqslant 400, & y=\dfrac{4(x-100)}{3}\times 40\,; \\ \text{when} & 400<x\leqslant 3{,}900, & y=x(2\cdot 4\sqrt{x}-8)\,; \\ \text{and, when} & 3{,}900<x, & y=3{,}900\times 141\cdot 88+216(x-3{,}900). \end{array}\right\}$$

[1] It is, of course, possible that, if Mr. Fadden's proposals had been adopted, the legality of the War-time Loan Contribution Act, 1941, might have been challenged in the High Court, as in fact if not in name imposing a Federal income tax which differentiated between citizens of the different States.

For a person with dependent wife, actual income £x, National Contribution y pence, and contributory income £C, these results are replaced by the following[2] :

$$\left.\begin{array}{lll} \text{when} & 0<x\leqslant 150, & C=0\ ; \\ \text{when} & 150<x\leqslant 450, & C=\dfrac{4(x-150)}{3}\ ; \\ \text{and, when} & 450<x, & C=(x-50). \end{array}\right\}$$

$$\left.\begin{array}{lll} \text{Also, when} & 0<x\leqslant 150, & y=0\ ; \\ \text{when} & 150<x\leqslant 450, & y=\dfrac{4(x-150)}{3}\times 40\ ; \\ \text{when} & 450<x\leqslant 3{,}950, & y=(x-50)[2\cdot 4\sqrt{(x-50)}-8], \\ \text{and, when} & 3{,}950<x, & y=3{,}900\times 141\cdot 88+216(x-3{,}950). \end{array}\right\}$$

Similarly, for a person with dependent wife and one dependent child, we have :

$$\left.\begin{array}{lll} \text{When} & 0<x\leqslant 200, & C=0\ ; \\ \text{when} & 200<x\leqslant 500, & C=\dfrac{4(x-200)}{3}\ ; \\ \text{and, when} & 500<x, & C=(x-100). \end{array}\right\}$$

$$\left.\begin{array}{lll} \text{Also, when} & 0<x\leqslant 200, & y=0. \\ \text{when} & 200<x\leqslant 500, & y=\dfrac{4(x-200)}{3}\times 40\ ; \\ \text{when} & 500<x\leqslant 4{,}000, & =y(x-100)[2\cdot 4\sqrt{(x-100)}-8], \\ \text{and, when} & 4{,}000<x, & y=3{,}900\times 141\cdot 88+216(x-4{,}000). \end{array}\right\}$$

3. Return now to the National Contribution of a person whose *contributory income* is £x. Let the National Contribution be y pence.

Then, when $0<x\leqslant 400$, $y=40x$;
when $400<x\leqslant 3{,}900$, $y=x(2\cdot 4\sqrt{x}-8)$;
and, when $3{,}900<x$, $y=141\cdot 88\times 3{,}900+216(x-3{,}900)$.

Thus y is a continuous function of the positive variable x.

Also, when $0<x\leqslant 400$, $\dfrac{dy}{dx}=40$;

when $400<x\leqslant 3{,}900$, $\dfrac{dy}{dx}=3\cdot 6\sqrt{x}-8$;

and, when $3{,}900<x$, $\dfrac{dy}{dx}=216$.

The graph of $\dfrac{dy}{dx}$ indicates the amount of the contribution made by each successive £ of contributory income. This is in fact equal to the area between the ordinates at x and $x+1$, the curve and the axis of x. It will be seen that in the graph there is a change from 40 to 64, as we pass through 400, and from 216·82 to 216 as we pass through 3,900. To these correspond a jump of about 24 pence in the sum contributed by the 401st £ as compared to that by the 400th, while the flat rate of 216 pence in the £ on the excess over £3,900 is indicated by the amount contributed by the 3,900th £.

The curve given by the equation $y=a\sqrt{x}+b$ is a branch of a parabola, with its axis parallel to the axis of x.

In the graph referred to above, this parabola would have a very slight curvature.

The Income Tax Rates of the Fadden Budget (1941–42).

4. It will not be necessary to deal at such length with the income tax rates proposed in the Fadden budget, 1941–42. The statutory exemption remained as before, namely £200 diminished by £1 for every £1 by which the assessable income exceeds £200, and thus vanishing at £400.

[2] There was an allowance of £50 for dependent wife and each child.

With the notation of my earlier paper, let the amount of the tax on a taxable income of £x be T pence.

Then, for income derived wholly from personal exertion, the relation between T and x is as follows:

When $0<x\leqslant 400$, $T=15x$;

$400<x\leqslant 3{,}350$, $T=x(1\cdot 8\sqrt{x}-21)$.

This gives, when $x=3{,}350$, $T/x=83\cdot 1825$.

Then, when $3{,}350<x$, $T=83\cdot 1825\times 3{,}350+135(x-3{,}350)$.

Or, in words:

If the taxable income does not exceed £400, the rate of tax for every £ of taxable income shall be 15 pence.

If the taxable income exceeds £400 and does not exceed £3,350, the rate of tax for every £ of taxable income shall be $(1\cdot 8\sqrt{x}-21)$ pence.

If the taxable income exceeds £3,350,

(*a*) The rate of tax for every £ of taxable income up to and including £3,350 shall be $83\cdot 1825$ pence; and

(*b*) the rate of tax for every £ of taxable income in excess of £3,350 shall be 135 pence.

For income derived wholly from property, the corresponding equations are:

When $0<x\leqslant 400$, $T=18x$;

when $400<x\leqslant 2{,}750$, $T=x(2\sqrt{x}-22)$.

This gives, when $x=2{,}750$, $T/x=82\cdot 8809$.

Then, when $2{,}750<x$, $T=82\cdot 8809\times 2{,}750+135(x-2{,}750)$.

Or, in words:

If the taxable income does not exceed £400, the rate of tax for every £ of taxable income shall be 18 pence.

If the taxable income exceeds £400 and does not exceed £2,750, the rate of tax for every £ of taxable income shall be $(2\sqrt{x}-22)$ pence.

If the taxable income exceeds £2,750,

(*a*) the rate of tax for every £ of taxable income up to and including £2,750 shall be $82\cdot 8809$ pence; and

(*b*) the rate of tax for every £ of taxable income in excess of £2,750 shall be 135 pence.

The remarks in §3 as to the graph of $\frac{dy}{dx}$ can be adapted to the graph of $\frac{dT}{dx}$ in this section. It will be seen that there is a "jump" at 400 in the amounts paid by the 400th and 401st pounds and that the flat rate of 135 pence in the £ on each £ of the excess is indicated by the amount paid by the last £ of the ascending progression.

The Income Tax Rates of the Revised Budget (1941–42).

5. Parliament reassembled on November 13 after a short recess to allow the new Government to prepare its budget. Almost half of the financial year had expired and the figures for the expenditure, both on war and civil purposes, set down by their precedessors were in the main adopted. But it was intended to review the budget position early in the new year and to bring down a supplementary budget to provide for any additional finance that might be required.

The new Treasurer (Mr. Chifley) proposed to leave the rates of income tax[3] unchanged on taxable incomes from personal exertion not exceeding £1,500 and on

[3] See §10 of my former paper; but on p. 39, line 3 from below, 1939–40 should read 1940–41. The same correction has to be made on p. 38, line 10 from below.

property incomes not exceeding £1,200. On incomes above these figures, there was to be a considerable increase in the tax. On earned income the progression was to be continued up to £2,500, and on property income up to £2,000. The 2,500th £ of earned income and the 2,000th £ of property income would then pay just under 200 pence. On the excess over £2,500 in the one case and over £2,000 in the other, there was to be a flat rate of 16s. 8d. in the £.

With the usual notation, the scale of rates is as follows :

Earned Income.

When $0 < x \leqslant 400$, $R = 16$.

When $400 < x \leqslant 2{,}500$, $R = \frac{x}{25}$.

When $2{,}500 < x$, on the first £2,500 $R = 100$ and on the excess over £2,500 there is a flat rate of 16s. 8d. in the £.

Property Income.

When $0 < x \leqslant 400$, $R = 20$.

When $400 < x \leqslant 2{,}000$, $R = \frac{x}{20}$.

When $2{,}000 < x$, on the first £2,000 $R = 100$ and on the excess over £2,000 there is a flat rate of 16s. 8d. in the £.

As high incomes were subject to a severe State income tax, rising in the highest taxing State to 8s. in the £ on the excess over £8,000, this scale made it quite possible that on some incomes, even allowing for the deduction of State income tax in arriving at the taxable income for Federal purposes, the combined taxes might amount to as much as 18s. in the £. Also a flat rate of 16s. 8d. in the £ in the Federal tax starting as early as the excess over £2,500 (or £2,000) hardly complies with the principle of ability to pay. However the proposals were adopted, with some protests from the Opposition that low incomes were not being taxed as much as in the circumstances they ought to be.

Parliament adjourned on November 27 on the understanding that it would be called together again whenever the situation made such a step necessary.

6. This call came much sooner than was expected, for on December 8 Australia was at war with Japan. Parliament met again on December 16. In this place we are concerned only with the new proposals for increased taxation. An increase was clearly necessary and now the lower incomes were to be called upon as well as the higher. The increase was made in the form of a " War Tax ", which, in the case of persons without dependants, began as low as on wages of £3 a week. This tax was assessed, roughly speaking, on actual income remaining after current Federal income tax had been deducted and the scale was a simple one :

When $156 < x \leqslant 162$, $R = 6$
$162 < x \leqslant 168$, $R = 6 \cdot 25$
$168 < x \leqslant 174$, $R = 6 \cdot 5$
$174 < x \leqslant 180$, $R = 6 \cdot 75$
$180 < x \leqslant 186$, $R = 7$
} pence in the £.

And so on, a rise of $\frac{1}{4}$d. for every additional £6 of income, so that, when we come to £276 to £282, $R = 11$, and at £294 to £300, $R = 12$.

Every income over £300, subject to the proviso about the deduction of Federal income tax already paid, was to pay a War Tax of 1s. in the £.

7. With this new tax the difficulties arising from the two independent taxation authorities in the field of income tax became so serious, both in the case of individuals and companies, that it was clearly absolutely necessary to straighten out the taxation system. The Government had come to see that nothing short of complete control by the Commonwealth during the war would meet the huge demands that had to be faced. National needs had to take precedence over State rights. On February 23, 1942, the Federal Treasurer appointed a committee of three persons to consider the question of the Commonwealth being the sole taxing authority in the field of income tax for the duration of the war, and of payment of compensation to the States by way of grants for the loss of revenue this would entail to them. The chairman was the Professor of Economics in the University of Sydney, Professor R. C. Mills, already chairman of the Commonwealth Grants Commission ; the other members were Mr. J. H. Scullin, M.P., a former Labour Prime Minister and Treasurer, and a public accountant, Mr. E. S. Spooner, M.P., a former Treasurer of N.S.W.

This committee submitted its report on March 28 and made unanimous recommendations, of which it will be sufficient to quote the following :

" 1. The committee recommends that for the duration of the war and for one year afterwards, the Commonwealth should be the sole taxation authority in the field of income tax.

" 2. A scheme of uniform income taxation imposed by the Commonwealth should operate from July 1, 1942, in respect of the income year 1941–1942, and the States should be compensated on retiring from the field of income taxation.

" 3. The Commonwealth should, after June 30, 1942, administer the income tax laws of the States for the completion of assessments and the collection of arrears in respect of income years prior to 1941–1942.

" 4. The committee is impressed with the urgency of this reform, particularly under war conditions. The expeditious and effective raising of revenue assumes greater importance during a period of national crisis. Income tax is the main source of revenue[4] from which the Commonwealth finances war expenditure, and that source is limited. The Commonwealth, therefore, should not be hampered by State laws, which prevent the fullest exercise of taxation powers essential to the nation at war. The presence in the field of six States imposing eleven taxes on income at widely different rates restricts the power of the Commonwealth in raising revenue from income taxation."

On the question of compensation to each of the States, the Committee recommended as a basis the average collections from taxes on income in each State in the two war-time financial years, 1939–1940 and 1940–1941.

It gave as an appendix to its report a scale of rates for the new Federal income tax on individuals designed to produce, with as little change as practicable, substantially the same revenue as was received in the previous financial year from the combined Federal and State taxes on income, and it made recommendations regarding the means of introducing a uniform system of company taxation with minimum change.

8. For the second time in twelve months a Federal Government now approached the State Governments in an attempt to find a solution to the competition between Commonwealth and State governments in the income tax field. The Federal Government was ready to accept almost all the recommendations of the committee, but at a conference with the State Premiers their proposals were rejected on the plea that they were an invasion of State rights,

[4] The War Loans and Savings Certificates must not be forgotten.

and the States put forward no acceptable alternative for a solution of the problem. The Government then decided to go forward with their plan and to submit to Parliament, which had been meeting at intervals since February 20, legislation to give effect to it.

This legislation took the form of four Bills, placed before the House of Representatives on May 15, namely the *Income Tax (War-time Arrangements) Bill*, 1942) ; *States Grants (Income Tax Reimbursements) Bill*, 1942 ; *Income Tax Assessment Bill*, 1942 ; and *Income Tax Bill*, 1942.

The first named provided machinery for the temporary transfer to the Commonwealth of the trained staff and the accommodation and equipment used by the States for the purpose of collecting income tax.

As to the second, it had been suggested to the Governments of the States that they refrain from imposing taxes on income for the duration of the war and one year thereafter. The Government had undertaken to make to each State agreeing to that proposal a grant of financial assistance to compensate for the income tax revenue lost, and the States Grants Bill contained a schedule setting out the amount it was proposed to grant. The average income tax collections of the State in the previous two years had been taken as a basis. The grants named in the Bill could be increased on a claim being made by a State that its financial circumstances were such as to warrant an increase. The Commonwealth Grants Commission would deal with such an application.

The *Income Tax Assessment Bill*, 1942, made changes in earlier assessment Acts rendered necessary by the introduction of the uniform tax.

The *Income Tax Bill*, 1942, contained the schedules for the rates of income tax on individuals and companies.

All these measures after some discussion in both Houses were finally adopted with some slight amendments at the end of May and Parliament adjourned on June 4 after a session which will without doubt have far-reaching consequences on the constitutional development of the Commonwealth.

It will be sufficient here to record that the legality of these Acts was challenged by some of the State Governments, but the High Court in July, by a majority judgment, upheld the validity of all of them. The State Governments then intimated to the Commonwealth their willingness to vacate the field of income tax during the period of the operation of the plan.

The Uniform Tax on Individual Incomes Received in the Year Ending June 30, 1942.

9. Before giving details of the sections of the Income Tax Act, 1942, which deal with incomes from individuals, two or three explanatory sentences are needed. The statutory exemption (better called deduction) is withdrawn, but no tax is levied on individuals whose incomes do not exceed £156. When the taxable income exceeds £156 and does not exceed £170, the amount of the tax is half of the excess over £156, when this is less than the sum given by the formulæ of the schedule, after allowing for all rebates. The concessional deductions, which were formerly applied to the income itself, are now replaced by rebates. State income tax paid in the year ending June 30, 1942, is not allowed as a deduction. The old arrangement is continued for incomes derived partly from personal exertion and partly from property.

The long statement in the schedule (divisions A and B) can be replaced by the following, where the amount of the tax on a taxable income of £x is T pence.

Taxpayer without Dependants.[5]

Earned Income.

When $150 < x \leqslant 200$, $T = 1{,}200 + (x-150)\left[8 + \frac{12}{100}(x-150)\right]$.

When $200 < x \leqslant 250$, $T = 1{,}900 + (x-200)\left[50 + \frac{8}{100}(x-200)\right]$.

When $250 < x \leqslant 600$, $T = 4{,}600 + (x-250)\left[58 + \frac{2}{100}(x-250)\right]$.

When $600 < x \leqslant 2{,}500$, $T = 27{,}350 + (x-600)\left[72 + \frac{33}{1{,}000}(x-600)\right]$.

When $2{,}500 < x \leqslant 4{,}000$, $T = 283{,}780 + (x-2{,}500)\left[198 + \frac{6}{1{,}000}(x-2{,}500)\right]$.

When $4{,}000 < x$, $T = 593{,}780 + 216(x-4{,}000)$.

Income from Property.

When $150 < x \leqslant 200$, $T = 1{,}500 + (x-150)\left[10 + \frac{15}{100}(x-150)\right]$.

When $200 < x \leqslant 250$, $T = 2{,}375 + (x-200)\left[62{\cdot}5 + \frac{1}{10}(x-200)\right]$.

When $250 < x \leqslant 600$, $T = 5{,}750 + (x-250)\left[72{\cdot}5 + \frac{25}{1{,}000}(x-250)\right]$.

When $600 < x \leqslant 2{,}100$, $T = 34{,}187{\cdot}5 + (x-600)\left[90 + \frac{41{\cdot}25}{1{,}000}(x-600)\right]$.

When $2{,}100 < x$, $T = 262{,}000 + 216(x-2{,}100)$.

10. These relations between T and x correspond to the following scheme:

Earned Income. There is a flat rate of 8 pence in the £ up to £150. The 151st £ pays 8·12 pence and on each successive £ up to the 200th the charge is increased by 0·24 pence, so that the 200th £ pays 19·88 pence.

The 201st £ pays 50·08 pence, and on each successive £ up to the 250th the charge is increased by 0·16 pence, so that the 250th £ pays 57·92 pence.

The 251st £ pays 58·02 pence, and on each successive £ up to the 600th the charge is increased by 0·04 pence, so that the 600th £ pays 71·98 pence.

The 601st £ pays 72·033 pence, and on each successive £ up to the 2,500th the charge is increased by 0·066 pence, so that the 2,500th £ pays 197·367 pence.

The 2,501st £ pays 198·006 pence, and on each successive £ up to the 4,000th the charge is increased by 0·012 pence, so that the 4,000th £ pays 215·994 pence.

On the excess over £4,000 there is a flat rate of 18 shillings in the £.

Property Income. There is a flat rate of 10 pence in the £ up to £150. The 151st £ pays 10·15 pence, and on each successive £ up to the 200th the charge is increased by 0·3 pence, so that the 200th £ pays 24·85 pence.

The 201st £ pays 62·6 pence, and on each successive £ up to the 250th the charge is increased by 0·2 pence, so that the 250th £ pays 72·4 pence.

[5] It should be noted that with the proviso that incomes not exceeding £156 are to pay no tax and that those from £156 to £170 are not to pay more than half the excess over £156 this statement has to be read as affecting only incomes above £170.

The 251st £ pays 72·525 pence, and on each successive £ up to the 600th the charge is increased by 0·05 pence, so that the 600th £ pays 89·975 pence.

The 601st £ pays 90·04125 pence, and on each successive £ up to the 2,100th the charge is increased by 0·0825 pence, so that the 2,100th £ pays 213·70875 pence.

On the excess over £2,100 there is a flat rate of 18 shillings in the £.

The awkward figures in the property rates are due to the fact that up to £2,100 the charge on property income is to be greater by one-quarter than that on the same earned income.

If the progression had been continued up to £2,125, the charge on the 2,125th £ would have been 215·77125 pence and the flat rate of 18 shillings in the £ on the excess would not have entailed the " jump " that occurs above at £2,100.

The increase in the charge at £200 in earned income from just under 1s. 8d. on the 200th £ to just over 4s. 2d. on the 201st, and on property income from just under 2s. 1d. on the one to about 5s. 3d. on the other, has been made so that incomes below £200 will be taxed more leniently.

11. With the Commonwealth the sole taxing authority on income, one might expect under present conditions a very severe, but simple and reasonable, graduated tax. The uniform tax described in the previous section is certainly severe, but it is not simple, and it might be questioned if in all respects it is reasonable. The difficulty has arisen because it has been thought well for the financial year ending 1942–43 dealing with income received in the year ending June 30, 1942, to adopt a scale which will, with as little change as practicable, bring in revenue equivalent to the combined Federal and State taxes on income for the previous financial year. With the State taxes on income varying so much in the different States, both on low and high incomes, any scale that would correspond approximately to the combined Federal and State taxes must be a complex one. It is to be hoped that, when the rates of tax for the next financial year are being considered, a simpler and in many respects a more equitable scale will be devised. My own preference is for successive stages in which the charges on each £ form arithmetical progressions with common differences diminishing as we proceed, so that the graph of $\frac{dT}{dx}$ is a set of straight lines with diminishing gradients, tending to zero as we approach the flat rate. There should be no " jumps " as we proceed from one straight segment to the next. It is this principle that has been adopted in the scale described above, but the " jump " at £200 is a blot, and all the gradients do not diminish as we proceed.

Also, it seems a pity that the statutory deduction has been cut out. The arrangement at the point where income becomes taxable in the uniform tax scale is apparently due to the influence of the State wages taxes.

Added April 24, 1943.

12. I take the opportunity afforded by the correction of the proofs of this paper to add a short note on the Income Tax Act 1943, which became law about the middle of March. In the accompanying Income Tax Assessment Act £104 was substituted for £156 of the 1942 Act as the point where exemption from tax of individuals without dependants ceases, but along with these Acts there was passed a National Welfare Fund Act 1943, which provides that from July 1, 1943, there is to be paid into a National Welfare Fund out of Consolidated Revenue an annual sum of (*a*) £30,000,000, or (*b*) a sum equal to one-quarter of the total collections each year from income tax on individuals, which ever may be the smaller. This Act may be supposed to compensate taxpayers of low and moderate incomes for the quite severe burden of tax they have now to carry under the provisions of the 1943 Act, which deals with incomes received

in the year ending June 30, 1943. Payments on account of this tax by weekly instalments began on April 1.

For the statement in §9 above, there has to be substituted the following:

Taxpayer without Dependants.

Earned Income.

When $0<x\leqslant 300$, $T=600+(x-100)\left[30+\frac{165}{1,000}(x-100)\right]$.

When $300<x\leqslant 1,000$, $T=13,200+(x-300)\left[96+\frac{1}{100}(x-300)\right]$.

When $1,000<x\leqslant 2,000$, $T=85,300+(x-1,000)\left[110+\frac{33}{1,000}(x-1,000)\right]$.

When $2,000<x\leqslant 3,000$, $T=228,300+(x-2,000)\left[176+\frac{15}{1,000}(x-2,000)\right]$.

When $3,000<x\leqslant 5,000$, $T=419,300+(x-3,000)\left[206+\frac{4}{1,000}(x-3,000)\right]$.

When $5,000<x$, $T=222x-262,700$.

Income from Property.

When $0<x\leqslant 200$, $T=600+(x-100)\left[30+\frac{165}{1,000}(x-100)\right]$.

When $200<x\leqslant 300$, $T=5,250+(x-200)\left[75\cdot5+\frac{24}{100}(x-200)\right]$.

When $300<x\leqslant 1,000$, $T=15,200+(x-300)\left[123\cdot5+\frac{1}{100}(x-300)\right]$.

When $1,000<x\leqslant 2,000$, $T=106,550+(x-1,000)\left[137\cdot5+\frac{34}{1,000}(x-1,000)\right]$.

When $2,000<x\leqslant 5,000$, $T=278,050+(x-2,000)\left[205\cdot5+\frac{275}{100,000}(x-2,000)\right]$

When $5,000<x$, $T=222x-190,700$.

13. These relations between T and x correspond to the following scheme:

Earned Income. There is a flat rate of 6 pence in the £ up to £100. The 101st £ pays 30·165 pence, and on each successive £ up to the 300th £ the charge is increased by 0·33 pence, so that the 300th £ pays 95·835 pence.

The 301st £ pays 96·01 pence, and on each successive £ up to the 1,000th £ the charge is increased by 0·02 pence, so that the 1,000th £ pays 109·99 pence.

The 1001st £ pays 110·033 pence, and on each successive £ up to the 2,000th £ the charge is increased by 0·066 pence, so that the 2,000th £ pays 175·967 pence.

The 2,001st £ pays 176·015 pence, and on each successive £ up to the 3,000th £ the charge is increased by 0·03 pence, so that the 3,000th £ pays 205·985 pence.

The 3,001st £ pays 206·004 pence, and on each successive £ up to the 5,000th £ the charge is increased by 0·008 pence, so that the 5,000th £ pays 221·996 pence.

On the excess over £5,000 there is a flat rate of 18s. 6d. in the £.

Property Income. Up to £200 the tax is the same as for earned income, and the 200th £ pays 62·835 pence.

The 201st £ pays 75·76 pence, and on each successive £ up to the 300th £ the charge is increased by 0·48 pence, so that the 300th £ pays 123·26 pence.

The 301st £ pays 123·51 pence, and on each successive £ up to the 1,000th £ the charge is increased by 0·02 pence, so that the 1,000th £ pays 137·49 pence.

The 1,001st £ pays 137·534 pence, and on each successive £ up to the 2,000th £ the charge is increased by 0·068 pence, so that the 2,000th £ pays 205·466 pence.

The 2,001st £ pays 206·50275 pence, and on each successive £ up to the 5,000th £ the charge is increased by 0·0055 pence, so that the 5,000th £ pays 221·99725 pence.

On the excess over £5,000 there is a flat rate of 18s. 6d. in the £.

Owing to the proviso that there is to be no tax on incomes not exceeding £104 and a special arrangement for incomes not exceeding £113, this analysis must be read as affecting only incomes above £113.

It will be seen that some of the criticisms in §11 of the scales in the 1942 Act do not apply to this one, and it is satisfactory that the flat rate starts at a later stage in both kinds of income. The method of differentiating between earned and property income and the very heavy burden put upon the latter after £200 is reached as compared with earned income, till the flat rate starts at £5,000 in both, may be considered defects, and on composite incomes, partly earned and partly property, the method of treatment that has been followed since 1916 leads to absurd results in some cases. It is to be hoped that in time further alterations may be made.

GALILEO AND NEWTON: THEIR TIMES AND OURS.*

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In order to appreciate the magnitude and the significance of the contribution made by a great leader of the past in any field of human endeavour, we must study his achievement in relation to the times in which he lived, we must see to what extent he depended on past work, what were the state of knowledge and the attitude of his contemporaries, and what influence he had on them and their successors. In speaking of the two men to whom we pay tribute tonight, I am keeping this in mind and shall concern myself more with their relations to the times in which they lived and worked, and with the bearing of their experiences on scientific practice and thought today than with the detailed tale of their achievements, which in any case could not be given adequately in the time available.

Galileo, who was born in Florence on 15th February, 1564, came into a world that was ready for his genius, his persistent search for truth and his valiant efforts for its establishment. Although, long before his time, there had been occasional protests against the unquestioning belief in the teachings of the past and pleas for the test of experiment from men such as Roger Bacon, in the 13th century, and Nicolas de Cusa in the 15th, these were unheeded and the real starting point of modern science came in 1453, when Copernicus completed his book on *The Revolutions of the Heavenly Bodies.*

When Galileo's scientific career began the theory of Copernicus had received some attention and support and there were a few active workers in experimental science such as William Gilbert in England (1540–1603) whose systematic studies and experiments in magnetism are in keeping with the best traditions of the modern experimental method, and Simon Stevin in Holland (1548–1620). the founder of statics, to whom we owe the theorem of the parallelogram of forces and important work on the equilibrium and stability of floating bodies. Mention should also be made of Tycho Brahe (1546–1601) the astronomer who at Prague for many years made painstaking observations of the positions of the planets, supplying the material that Kepler (1571–1630) was later to use in the great generalisations, the laws of planetary motion known by his name. A few years senior to Galileo was Francis Bacon (1561–1626) who in his writings advocated the experimental method and laid down at length rules for scientific investigation. As a matter of fact, although he is better known than the others, he had little influence on scientific progress; Newton, for example, hardly mentions him while Bacon himself did not realise the value of the work of Gilbert and Galileo. In general it will be found, I think, that the philosopher who was not actually engaged in experimental science has made little contribution by his discussions in that field. The philosopher on experimental science might be compared with the old maid on the bringing up of children: each passes just criticism and gives excellent advice, but it is other people who do the things that really count.

* This address was delivered before the Society on October 7 in commemoration of the tercentenary of the death of Galileo (1564–1642) and the birth of Newton (1642–1727).

However, when we come to metaphysics, where the test of experiment cannot be applied, the strictures of the philosopher may be necessary because here the scientist often allows himself freedom from the self-discipline that he imposes in the performance and interpretation of his experiments. He is justified in his speculative mental excursions because the field that today is not susceptible to the test of experiment may be tomorrow—but it must be recognised that generally no special weight can be given to his opinions simply because he is a scientist. May I quote from a recent article by Stephen Leacock, entitled *Commonsense and the Universe.*

" When the scientist steps out from recording phenomena and offers a general statement of the nature of what is called ' reality ', the ultimate nature of space, of time, of the beginning of things, of life, of a universe, then he stands exactly where you and I do, and the three of us stand where Plato did—and long before him, Rodin's primitive thinker."

With this I cordially agree except for the suggestion at the beginning that the scientist should limit himself to recording phenomena. This is too like the views of Bacon. The scientist must use his observations ; they must be classified and he must seek an interpretation ; he must not stop at the stage of Tycho Brahe. Leacock and Bacon have no place for the inspired imagination, what Sullivan calls the ' physical insight ', that is the biggest factor in the greatness of a Newton, a Faraday, a Rutherford.

In spite of the work of Gilbert and Stevin and others of less note the traditions of the past centuries prevailed when Galileo's studies commenced. The science taught was that of the philosophers of ancient Greece, or rather the interpretation given it by the scholastic philosophers of the middle ages. All education being in the hands of churchmen—without them there had been none—it is not surprising that this science was given authority equal to that of the Scriptures. The Greeks were thinkers and reasoners never excelled ; some of them were observers of remarkable skill and thoroughness, but in general they were indifferent to experiment—they did not attempt to increase their knowledge by imposing conditions modifying observations. It seems natural that they would find greatest interest in profound speculations and discussions on the really big things, on the nature of the universe, on the ultimate structure of matter, on the infinities of space and time, while the laws of falling bodies and the commonplaces of mechanics would be treated as incidentals ; such minor topics are of absorbing interest only to those engaged in experiments relating thereto. This may be the reason why in the mechanics of the 16th century we find accepted statements that common experience must have shown to be incorrect, such as the assertion that bodies of unequal weight let fall from a height reach the ground in times inversely proportional to their weights. Aristotle's writings were interpreted to convey this, and it had to be accepted as the truth. On the other hand the Ptolemaic theory of a stationary earth was a working theory ; it enabled correct predictions of planetary phenomena to be made and on the face of it appeared more reasonable than the Copernican theory according to which the earth rotated daily about its axis. Surely speeds approaching 1,000 miles an hour should be noticeable ; an arrow fired vertically into the air should fall to the ground miles to the west if the surface had such velocity ; even if one jumped into the air, remaining off the ground for but a second or so, one should alight hundreds of yards to the west. These and like objections generally were taken to rule out the Copernican view.

Galileo from his student days was critical of the old teachings and convinced that they were wrong. He displayed from his youth keenness for experiment, and skill and ingenuity in the construction and use of apparatus. Securing favourable notice through several interesting inventions and for his mathematical knowledge, in 1589 he was appointed to a lectureship in the University

of Pisa ; three years later he went to Padua, where he held a professorship until 1610. During this period he displayed extraordinary activity in most branches of physics then studied. He made notable contributions in mechanics, including a detailed study of accelerated motion and quantitative examination of projectiles and falling bodies, proving the parabolic path, and he established the facts that we now know as Newton's first and second laws of motion. He carried out investigations on pendulums, pulley systems, specific gravities, pumps, was responsible for the beginning of thermometry, and, in magnetism, repeated and extended some of the experiments of Gilbert. He did important mathematical work, including a discussion on the geometry of the cycloid, and was keenly interested in practical problems, his military and geometric compass, an aid to calculations of diverse character, being an instance of this.

He was a remarkably able teacher and lecturer, and an interesting and entertaining talker, who made many friends, including a number of leaders in church and state. He took advantage of every opportunity of emphasising his opposition to the old doctrines and of urging the claims of the new beliefs. Thus after the appearance in 1604 of a striking new star he gave three public lectures that aroused wide interest ; in these he described the Copernican system and pointed to the *nova* as evidence against the unchanging character of the heavens, an essential feature of the old theory.

Many of our text-books and histories of physics tell us that, early in this period, in 1590 or thereabouts, Galileo carried out an epoch making experiment in which he dropped two unequal weights from the top of the leaning tower of Pisa. Their simultaneous fall to the ground, we read, rang the knell of the old beliefs, disproving Aristotle's assertion that the heavier one would reach the ground first, in one-tenth the time taken by the lighter if the weights were in the proportion of 10 to 1. This experiment was supposed to have been performed in front of a large university concourse but it is almost certain that if performed it was not as described in our histories. Professor Lane Cooper, who occupies a chair of English in Cornell University, provoked perhaps by the belittling of Aristotle, whom he rightly regards as one of the outstanding thinkers of all time, has made a careful examination of the story.* He points out that no mention of this " epoch-making " test was made until about 1654, when Viviani (1622–1703), the last and youngest of Galileo's pupils, related it in a biography of his master. Galileo in his own writings says what would happen in such an experiment but nowhere states definitely that it was performed by him. Lane Cooper reveals important discrepancies in the historical accounts ; the weights sometimes are ten pounds and one, in others one hundred and one ; the time is stated as the morning, though Viviani gives no information on this ; according to some the audience was the whole University, while others tell us that it consisted of the elderly conservative seniors, and we are told of their angry bewilderment at the result, but the outstanding point is that no publication occurred until more than 60 years later. I dwell on this at some length because it shows that we physicists who pride ourselves on the honesty of our work, on our meticulous attention to detail in experiment and record, do not carry this over into our histories. Apparently we feel that while truth may be stranger than fiction, a dash of fiction makes the story more worthwhile.

Lane Cooper goes further. He points out that it is difficult to establish the claim that Aristotle ever made such a statement as that credited to him. Words used by him may be given a meaning different from that intended and it must be remembered that in his day, and for that matter in Galileo's, words had not been invented to convey the ideas of impulse, momentum and the like. Further for the most part Latin translations of Aristotle were used, an extra

* Aristotle, Galileo, and the Tower of Pisa, Lane Cooper.

chance of uncertainty being thus introduced. However, there is little doubt that whatever Aristotle intended he was interpreted by the scholastics of the middle ages to have made the statement under discussion, and, as a matter of fact, Stevin did actually perform the experiment of letting two weights, one ten times as heavy as the other, fall from a height of about 30 feet. He records their simultaneous arrival on the ground as evidence against Aristotle.

This story illustrates two important points emphasised by the philosopher, Professor Collingwood, in his *Autobiography*: one, that in criticising and discussing work of the past we must read the original statements and not content ourselves with the versions of other writers; the second is that in interpreting writings of the past we must view them from the standpoint of the period, we must recall the state of knowledge and thought at the time, and remember that even the meanings of words and phrases might be different from those of today.

The physicist can find illustrations of the second point if he reads papers on heat written early in the 19th century when certain writers undoubtedly felt the truth of the first law of thermodynamics though it was not definitely stated until many years later. Similarly writings on atomic physics at the beginning of this century are rather puzzling if read from the standpoint of today.

There are probably other instances of "crucial" experiments described but never really performed. It is likely that many of the experiments on hydrostatics attributed to Pascal are simply propositions enunciated by him, consequences of the laws of hydrostatic pressure, instead of the statement of the laws being consequences of the experiments. Sir Humphrey Davy's experiment on the melting of ice when two blocks are rubbed together in ice-cold water is probably a statement of what would occur based on his correct interpretation of Rumford's classical observation.

To return to Galileo, in this first period he had established himself as the leader in science of his time and had provided a firm foundation for mechanics, that, without any other contribution, would have earned him a place among the great in science. The next stage commences with his observations with the telescope, the invention of which was reported to him in 1609. He soon worked out the theory of such an instrument and succeeded in constructing one, later making a number of ever-increasing power, one of which gave a magnification of 30 diameters. Early in 1610 he applied the telescope to the examination of the heavens and a few months later published the first account of his observations, recording a vast increase in the number of the stars, resolution of the milky way, detail in the moon indicating that it was of like nature to the earth, certainly that it had mountains and plains, the disc-like appearance of the planets, and, most important of all, tiny bodies close to Jupiter, that continued observation showed to be satellites circling round the planet.

A little later two other important discoveries were made. Saturn was found to be a complex body. What we recognise with our good instruments as the rings appeared to him as two bodies or excrescences on either side of the planet. He did not announce this discovery outright, because of earlier experience when others claimed credit for his findings, but gave it in the form of an anagram, 37 letters in a meaningless sequence, that later he revealed as "*Altissimum planetam tergeminum observavi*", that is, "I have discovered the most distant planet to be triple".

The second discovery was also put in the form of an anagram, "*Haec immatura a me jam frustra leguntur (o.y.)*", or "these immature things are read by me now in vain". Later he gave the solution "*Cynthiae figuras aemulatur mater amorum*" or "the mother of loves (Venus) rivals the figures of Cynthia (the moon)", or, in other words, Venus has phases like the moon. This discovery he regarded as evidence favouring the Copernican system, while the discovery

of the satellites of Jupiter revealed heavenly bodies that rotated round a body other than the earth and so formed an argument against the Ptolemaic theory.

At first this work brought Galileo great credit, and the Grank Duke of Tuscany appointed him to positions of honour in his household and in the University of Pisa that resulted in his leaving Padua for Florence. However, trouble soon commenced as the result of his enthusiastic advocacy of the Copernican theory the truth of which he thought must now be patent to all.

The opposition came mainly from churchmen, though among these there were varied views. Some were opposed by conviction—not only were the arguments mentioned earlier given, but more important still numerous scriptural texts were quoted indicating clearly that the earth was the stationary centre of the Universe. Others Galileo had antagonised by his ruthless method of debate and discussion, opponents of his views being subjected to cutting sarcasm and made to appear both incorrect and foolish, a most effective way of provoking enmity. Probably most of the leaders of the church, who included many friends and admirers of Galileo, would gladly have avoided the conflict that was being forced on them. Some appear to have believed that the new theory did not necessarily conflict with the teaching and authority of the church and others seem actually to have accepted it. However, opposition that is earnest, and even fanatical, must carry greater weight than lukewarm advocacy or indifference, and towards the end of 1615 he was denounced to the Inquisitor in Florence. Early in 1616 the matter was submitted to the Holy Office in Rome and a report was issued affirming the theory of the central sun to be foolish and absurd in philosophy and to be in contradiction to the Holy Scripture, while the theory of the moving earth with its diurnal motion was likewise condemned.

Galileo was admonished that he should renounce the condemned opinions, that he should no longer hold or defend them.

From this point we have less of experiment and observation by Galileo. There had not been systematic publication of the great volume of experimental work already performed by him and his main contributions henceforth consisted in the examination and discussion of his results, in preparing them for publication and above all in presenting convincingly the case for the new science. Nevertheless important new work does appear in the later part of his career, for example, but a few years before his death he made a discovery of major importance, the libration of the moon, and later still occupied himself with practical problems such as the determination of longitude at sea by means of lunar observations, and the application of the pendulum, the subject of his earliest research, to time-keepers. Further, there were new topics of discussion such as the tides and comets concerning which, however, views strenuously maintained by him have turned out to be quite incorrect.

The *Dialogues Concerning the Two Principal Systems of the World* occupied him from about 1623 to 1629 though already in 1610 he mentions the work as being in preparation ; a further period of several years then passed before he received permission to have it published. Urban VIII, who had been elected Pope in 1623, had long been a friend of Galileo and had not agreed with the verdict of 1616. He had said that belief in the Copernican theory was not heretical but rash and that it might even cease to be rash. Galileo, who never could understand the refusal of intelligent people to be convinced by the overwhelming evidence he could present, naturally felt that he might depart at least in the spirit if not in the letter from the injunction of 1616, and in the book presented indirectly a convincing case for the new system. It takes the form of a discussion on four successive days between three characters. Two of these, Salviati and Sagredo, named after deceased personal friends of Galileo, take the standpoint on the questions examined that Galileo himself would, while the third, Simplicio, named after Simplicius, a 6th century commentator on Aristotle,

advocates the old science and the Ptolemaic system. Galileo gives free rein to his sarcastic wit, and in the debates on the various topics discussed Simplicio always comes out badly and is made to appear ridiculous.

What Galileo considered one of the most important points in the book is a discussion on tides. Actually it is the weakest part because he was rather badly informed concerning the subject and developed a theory that is incorrect. He did not accept the view that had been advanced that the tides depended on the moon but found an explanation in terms of the diurnal rotation of the earth and its revolution about the sun ; he considered this to be an incontrovertible proof of the rotation of the earth and of the truth of the Copernican system. So important did this seem to him that he wanted to call the book " The Flux and Reflux of the Tides ".

To Galileo's disappointment he met considerable difficulty and delay in publication. The licensing authority demanded repeated revisions ; the Pope insisted on a change of title, omitting reference to tides, and directed that an argument should be included to the effect that even though the phenomena of the tides were consistent with the idea of the double movement of the earth that was not a proof that such movement existed—that God the Almighty in his omnipotence could ordain the tides on the stationary earth. This opinion is reasonable ; the fact that we are able to explain a phenomenon only on one hypothesis does not prove that such hypothesis is correct, it may rather reveal limitations of our knowledge or imagination. Unfortunately this statement, dictated by the Pope, Galileo puts into the mouth of Simplicio at the end of the book, affording a powerful weapon to his enemies, the suggestion that the fool of the piece is represented by the Pope.

The book, printed at last in 1632, immediately raised a storm. It is true that Galileo did not state that the new system was correct—it was advanced simply as an hypothesis—but the form given to the discussion was such as invariably to show that the old view was untenable and that its advocate made himself rather foolish. Another point was raised : Galileo thought that he had been forbidden only to hold or to defend the new system ; he had a letter from Cardinal Bellarmini to that effect, but a minute, unsigned, was produced by his opponents in which he was forbidden to hold, defend or *teach* the forbidden doctrine. The minute had been written in 1616 but the question was had it been communicated to Galileo. If so it would prohibit the discussion of the Copernican system even as an hypothesis, not necessarily claimed to be true. Evidently Urban VIII was persuaded that Galileo had been guilty of transgressing this minute and he appointed a commission to consider the book. It reported that Galileo had transgressed orders by asserting the mobility of the earth and the fixity of the sun, had incorrectly deduced an explanation of the tides from the non-existent double motion of the earth, and had been fraudulently silent concerning the command of the Holy Office in 1616 that he should not hold, teach or defend the hypothesis of the fixed sun and moving earth.

Galileo was next summoned before the Inquisition and in spite of the efforts of his friends was compelled to stand his trial and, as we know, then nearly 70 years old, stricken with illness, bewildered by the attitude of intelligent men and, as always, unable to realise how this work could make him anything but the orthodox Catholic that he felt he was, was persuaded to recant, to acknowledge the error of his views and his transgression of the order of 1616.

It is unnecessary to discuss this recantation or to speculate on the result of alternative action. The actual punishment imposed was relatively slight ; he had to recite the seven penitential psalms once a week for three years and was sentenced to virtual imprisonment, in effect simply a restriction on his place of residence and on his visitors, that was gradually relaxed, though he was never allowed to return to Florence. Possibly the greatest punishment was the

memory of the fact that he had yielded to the persuasion to abjure doctrines that he knew to be true.

It should be noted that opposition to the new doctrines was not restricted to the catholic church ; the protestant clergy was at least as emphatic. We are told, for instance, that at a protestant conference in Tübingen, Kepler was condemned for his support of the Copernican theory and had to take refuge with the Jesuits.

After the ordeal of his trial Galileo was yet to publish what some consider his finest work, the *Dialogues Concerning Two New Sciences*, completed in 1636 and published in Holland. It takes the form of the earlier dialogues ; the same three characters appear and the discussion is divided into four days, later a fifth and sixth being prepared. The topics in general relate to mechanics, and of special interest is the matter of accelerated motion and of the parabolic path of projectiles ; others are cohesion, friction, strength of beams, production of vacua, vibrations of sounding bodies, and in particular he discusses the fall of bodies of unequal weight dropped from a height. Most of the experimental work on which these discourses are based was performed in the first stage of his scientific career, that is before 1609. The tone is more friendly than in the earlier dialogues ; Aristotle's views are shown to be wrong but Simplicio is not made to appear as stupid as in the past.

Galileo's health was bad in these last years, and early in 1638 he became totally blind. Restrictions against visitors were then relaxed and he had visits from many notable people while his pupils, Viviani and Torricelli, were allowed to share his home. After a partial recovery, accompanied by a renewal of scientific activity, he became seriously ill towards the end of 1641 and died on 8th January, 1642.

Galileo had established experimental physics ; through his efforts and through his sufferings the new method of science became widely known and generally accepted in spite of the attempts to discourage the study of his writings. During the 17th century we find a steadily increasing number of workers, in his own country and abroad, some his pupils and all inspired or at least influenced by him. Torricelli and Viviani have been mentioned ; other well known names are Mersenne, Grimaldi, von Guericke, Pascal, Boyle, Huygens, Wren and Hooke, and, one who for a long time dominated scientific method and thought in France and elsewhere, Descartes. However, Descartes' theory of vortices, while plausible enough, was always inadequate, for example, it could not be reconciled with the laws of planetary motion. A new hypothesis should at least be consistent with known phenomena ; it is of value when it leads to wider knowledge of the facts of nature.

Soon after the middle of that century there was considerable interest in Science ; the new methods were adopted in the main and we find organised effort in the form of scientific institutions in various countries, such as the Royal Society of London. The way was prepared for Newton just as it had been for Galileo in an earlier generation.

Newton was a scientific genius. Superlatives on him are inadequate. A quotation of one line conveys the best idea :

" God said, ' Let Newton be ' and there was light."

He ranks as one of the greatest mathematicians the world has known, he is placed in the first order of experimenters and he possessed to a remarkable degree that indefinite quality that might be called inspired imagination that enabled him with uncanny skill to pick on the right explanation of his observations, to discriminate among the several possible, a rare gift of the highest importance in scientific progress.

Newton's work on gravitation, on mechanics, on light, the mathematical methods discovered and developed by him, are outstanding achievements any one of which would have earned him a place in the highest rank. He made important contributions in other fields of physics, heat and electricity for example. Yet only a relatively small portion of his life was devoted to this work ; Sullivan estimates that about one-third of his effective working time was spent on physics and mathematics, much of the rest being devoted to theological studies, historical research, chemistry and alchemy, fields that for considerable periods appeared more important to him.

He possessed exceptional powers of concentration that combined with his extraordinary ability enabled him to achieve results in remarkably short times. We read that one of the Bernoullis had propounded two problems concerning falling bodies, challenging mathematicians to give a solution in six months ; Leibnitz solved one but asked for a year for the second. Newton gave the solutions within 24 hours ; yet, apart from him, in mathematics there were giants in those days. However, accompanying this power of concentration there was a readiness to change the subject of his study. Early in his career when he had made great progress in his work on gravitation he left it, without any announcement or publication of what he had achieved, for work on light and colour, that in turn was dropped for the development of methods of grinding surfaces of lenses and mirrors.

Compared with Galileo we find many points of difference. Newton had the quality of the " lone hand " ; he was not concerned with the appreciation or understanding of his work by others ; left to himself much would not have been published and in general he made no attempt to write his papers in a form readily to be understood, in fact, sometimes he seems deliberately to have made them difficult. His lectures were few and poorly attended ; apparently he had little interest in this work. His investigations were made because they were of interest to himself, and he was indifferent to the praise of his admirers, though, like Galileo, he was irritated by what appeared stupid objections and misinterpretations.

Self-contained though he was, he formed a number of real friendships that he valued very highly, and intercourse with him had a great influence on contemporaries like Wren and Halley, while, as everyone recognises, his work has been the guide and inspiration of all physicists in the centuries that followed.

In his boyhood and youth Newton showed himself to be a good scholar with a wide range of interests. He had unusual mechanical skill and took great pleasure in making working models of various kinds. At Cambridge he got his first introduction to the study of mathematics and the opportunity of reading some of the work of science of that day, in particular Kepler's *Optics*. His early life at the University seems to have been much the same as that of others and it is even recorded that at this time he fell mildly in love, the only instance of anything approaching sex interest in his life.

The years 1665 and 1666, the two plague years, he spent in his mother's home in Lincolnshire (his father had died shortly before his birth) and in this period, working alone, his genius blossomed with extraordinary suddenness. In these two years he discovered the differential and integral calculus, worked out the essentials of his theory of gravitation, and carried out most of his investigations on colour and the composition of white light ; for the experimental work

in this last subject he had to make his own prisms and lenses and, for that, his own grinding and polishing machines. In all these fields a considerable amount of work was done later, but the essentials were completed in this short period, an extraordinary performance even had he been a mature investigator with life-long experience.

Soon after returning to Cambridge he communicated a mathematical paper on Analysis to Isaac Barrow, the Lucasian professor, who described it as a work of unparalleled genius, and on Barrow's retirement in 1669 his recommendation that Newton should be his successor was adopted. Newton was elected a Fellow of the Royal Society in 1672 and shortly after communicated a paper on the Composition of White Light.

Up to this time ideas concerning colour were vague; many held the Aristotlean view that colour was the result of a mixture of light and darkness, the actual colour depending on the proportions; Descartes had advanced another hypothesis in terms of pressure in the matter that, according to him, filled all space, but this, and other views propounded at the time, were indefinite and unsatisfying.

Newton, using prisms and lenses made by himself, performed numerous experiments on colour. Viewing red and blue papers through a prism, he saw that blue was refracted more; forming real images of strongly illuminated black threads on the coloured papers he found that the two could not be focussed on a screen for the one position of a lens. He sent a narrow beam of sunlight through a prism and projected a spectrum on a screen; the light from portion of this, passing through a small hole in the screen on to a second prism, was not dispersed but deviated, the deviation being greater for blue than red. By an inverted prism he combined the dispersed spectral beams again to form white light; by screening each half of the spectrum in turn he obtained complementary colours in this synthesis. He found the conditions necessary for a pure spectrum and rightly ranks as the pioneer of spectroscopy. The number, variety and significance of the experiments he performed on colour, on the nature of white light, on its analysis and on its synthesis remind us of the searching methods of Faraday, 150 years later.

Naturally he arrived at the facts of chromatic aberration and concluded that the refracting telescope could never be highly satisfactory. At the time there was not the variety of glasses made later and we can understand his belief that dispersion must always be proportional to deviation so that an achromatic combination did not suggest itself. As a result he developed the reflecting telescope.

He made systematic study of the colours of thin transparent films, a subject receiving attention from a number of workers at the time; we recall the well-known exhibit entitled Newton's rings.

At that period there was considerable interest in light and the theory of light; besides the new facts derived by Newton we must mention Grimaldi's diffraction experiments, the discovery of double refraction by Bartholinus, important work by Hooke on interference, and by Huygens on the explanation of reflexion and refraction by a wave theory.

Newton never succeeded in postulating a theory of light that satisfied himself; his, like others of the time, was necessarily indefinite, an inevitable result when so many new facts were being discovered and studied. He held that light was corpuscular in nature, but interference phenomena made him realise that there must be associated with it a periodicity of some kind. Like others at the time he believed in an ether, a subtle medium to which light and other phenomena were to be related but it was an ether different from that postulated in the 19th century.

Newton's experiments and views on light were published in his *Opticks* in 1704 but much was given in the paper presented to the Royal Society in 1672. In this, his first paper to the society, his matter was carefully prepared and clearly presented, but to his surprise it met objections and criticisms. His attitude of conveying the facts of nature simply as he observed them without reference to preconceived ideas, without asserting that he confirmed or disproved classical hypotheses was not understood ; the traditions of the past still prevailed to some extent. Further, there were accusations of carelessness and of misstatement, following which he was involved in a difficult and distressing correspondence, that in the end exhausted his patience so that after 1776 he made no further communication on light to the society and, in fact, shortly after seems to have given up his interest in physics and mathematics for several years during which he devoted himself chiefly to chemistry and the other subjects mentioned earlier.

Newton was unfortunate enough for considerable portions of his life to find himself involved in like bitter controversy with some of his fellow scientists, generally on questions of priority of discovery. Already at this time a dispute concerning the claims of Leibnitz to the discovery of the calculus had commenced ; this was destined to disturb him to the end of his days. To some extent Newton was to blame because of his indifference to publication ; he could not be similarly indifferent to unjust accusation of plagiarism and dishonesty, so that his rejoinders were often of a provocative nature tending to prolong the quarrels and to accentuate his own distress, with the result that on several occasions, as in 1676, he abandoned the work in hand for other interests.

However, more than anyone Robert Hooke is to be blamed for Newton's difficulties. Hooke, who was a few years older than Newton, was a physicist of outstanding ability who made notable contributions in many branches of the subject that should entitle him to an honoured place in the history of science. He was however a very vain man, jealous of the success of any of his contemporaries, and he gained an unenviable reputation as a carping critic and a persistent claimant for priority at the announcement of every new discovery. Hooke was indeed unlucky to have Newton among his contemporaries, a younger man who overshadowed him both in experimental and theoretical investigation, who solved, apparently with ease, problems that had puzzled him for years. He criticised Newton's optical work, questioned the correctness of his observations, asserted that he himself was the discoverer of the law of gravitation and that Newton had got the idea from him. Being skilled enough to discover one or two errors made by Newton in their correspondence concerning falling bodies in the earth's gravitational field, he took pains to dilate on this publicly in his consistent and resentful efforts to belittle his great rival. In the end the only remedy open to the sensitive Newton was to vacate the field.

The story of Hooke suggests that in assessing a man's value we should take into account the negative as well as the positive. Remarkable as are his achievements, are they not more than compensated by the loss of Newton to science for many years, because the other activities to which he turned, important as they seemed to Newton himself, were productive of little benefit to mankind ?

Time does not allow a detailed account of Newton's great work on gravitation. It was started during the plague years and dropped at about the same time as the optical work, though trying correspondence and discussion with Hooke continued for some time later. His interest was revived in 1684 by Halley to whom he announced, in reply to a question, that he had proved years before that the inverse square law of attraction would account for the elliptical orbits of the planets, a proof that had been sought by Wren, Hooke, Halley and others. He again obtained the solution that he had lost in the interval, and, stimulated by Halley, recovered his former enthusiasm with the result

that after less than two years' intensive work he produced the monumental treatise, the *Principia*, that established him as the founder of theoretical or mathematical physics. In this comprehensive collection of propositions in mechanics and gravitational theory we find thoroughness and completeness corresponding with those of the experimental work on light and colour, and not the least remarkable feature is the fact that most of these were worked out in about 17 months. The actual publication is due mainly to Halley ; he induced Newton to do the work and made himself responsible for the cost, an attitude in marked contrast to that of Hooke, who still insisted that Newton stole his ideas. As a matter of fact Hooke and many others had suggested that the inverse square law held but were unable to prove it.

The *Principia* was eagerly read but it was not until the second half of the 18th century that it bore full fruit when the great French mathematical physicists, having at last dropped the Cartesian theory, accepted and developed the Newtonian method. Of course all the progress of the 19th century, in light, electricity, heat, sound, in every branch of physics, is really an extension of Newton's work.

After the publication of the *Principia*, Newton again gave up his scientific work and in fact little more was done by him apart from the publication of his *Opticks* in 1704, after Hooke's death, and the preparation of later editions of the *Principia*.

This withdrawal from active participation in science was probably due to a series of irritating quarrels with Flamsteed, the Astronomer Royal, that went on intermittently, and on various subjects, from 1691 for more than twenty years, and to a revival and intensification of the controversy with Leibnitz and his supporters, mentioned earlier.

For a time Newton represented the University of Cambridge in the English parliament, and later occupied the position of Warden and then Master of the Mint, where he did good work in instituting greatly needed reforms. There was an unhappy period in about 1693 when he was mentally unbalanced, a state revealed by amazing letters containing painful reproaches and accusations sent to Locke and other good friends.

In 1703 he was elected President of the Royal Society and was re-elected each year until his death, though he took no active part in the control of the society.

During his later years he devoted himself largely to religious studies and bible interpretation, in which he revealed strong feeling against the Roman Catholic Church, finding numerous unpleasant references to it in the book of Daniel, and shortly before his death he prepared a great volume on Scriptural Chronology, but on these works we need not dwell as they do not affect our appreciation of his greatness.

It is pleasant to recall that his last recorded activity was associated with Science : on 28th February, 1627, he presided at a meeting of the Royal Society a few days before he was stricken by the illness from which he died on 20th March.

Today how are we to regard the work of Newton and Galileo ? We have to agree that many of their conclusions are not correct. Newton's theory of light is inadequate and widely different from that of our time, his idea of the absolute is discarded, and his mechanics are but a special case of a more general system. Galileo's struggle may appear futile because now we realise that we may take the earth, or the sun, or any other body, as our standard of reference as we find it convenient, and in fact I wonder whether ever any Copernican was so consistent as to refrain from speaking of sunrise and sunset.

What I wish to emphasise is that these men did what the world was ready for at the time ; it took 200 years of scientific progress, based on Newton's work and inspired by his example, before we were prepared for the new concept of Planck and before there was need for the generalization of Einstein. Had Newton advanced such modern views they would have been no more than metaphysical speculation, incapable then of experimental verification and leading nowhere. The great lesson taught by Galileo and Newton is that such speculation is of secondary importance.

Galileo's struggle, at the time, appeared to be for the acceptance of one of two conflicting systems of the universe, but now we know that in fact it was for the establishment of freedom of thought. His defeat was victory, a victory without which progress had not been possible.

Today, as 300 years ago, great problems are still unsolved, the questions of science and religion, faith and reason. Galileo had to fight against the faith that excluded reason ; today it may be necessary to fight against a reason that denies the claims of faith.

Something might be found common among the widely divergent views on these problems, common to the extreme materialist and to him who puts full trust in revealed religion. Actually all have faith of some kind, even if it is faith only in human reason, but, more important, we all *know* that our universe is one of law and order. I remember, years ago, reading of Kepler's first paper in which, supporting the Copernican theory, he maintained the thesis that, besides the earth, there could be but five planets, basing this on the fact that there were but five regular solids, and developing a scheme of spheres, containing the orbits, inscribed in and circumscribing the polyhedra taken in a certain order. At the time I regarded this with scorn and wondered at the friendly reception it received from the wise Galileo and the methodical Tycho. Today I regard it as a manifestation of our desire for order and law, of our search for relationships between the phenomena of nature.

Perhaps the main difference between our extremists is that the one assumes that the Universe, once started, goes on inevitably in accordance with laws, unchanging and definite, while the other assumes the possibility of the laws being suspended, presumably at the will of a divine Guide and Controller. In the principle of indeterminism it might be claimed that modern physics gives an indication in this direction, and in connection with recent developments in atomic and cosmic physics the suggestion has been made that under certain conditions the law of the conservation of energy may not hold.

Another difference is between their methods of describing the start of the Universe. The one says, " In the beginning God created the heaven and the earth " ; G. K. Chesterton would call this commonsense. The other usually assumes either an initial chaos of primitive entities that for some reason commence to group themselves, developing into the complex structures we know, or an initial vast single molecule that divides, eventually to form the bodies that make up the world. These suggestions are as difficult to understand as the first but the word " God " is avoided and they are called rational.

However, debate on these matters is irrelevant. The greatness of Galileo and Newton is not conditioned by their religious beliefs. They were regarded as giants in their own times ; we, at a distance of three centuries, endorse this view ; we see them towering above their fellows, and approached but rarely in the intervening years. I am not alone in maintaining that, measured by their achievement, or by their influence on the progress of civilisation, they rank higher than the greatest of the kings, statesmen, captains, round whom our histories are written.

On this note I end with a quotation from an appreciation of science, *Wintry Delights*, by the late Poet Laureate, Robert Bridges, a quotation fitting the occasion and the times in which we live :

> What was Alexander's subduing of Asia, or that
> Sheep-worry of Europe, when pigmy Napoleon enter'd
> Her sovereign chambers, and her kings with terror eclips'd ?
> His footsore soldiers inciting across the ravag'd plains,
> Thro' bloody fields of death tramping to an ugly disaster ?
> Shows any crown, set above the promise (so rudely accomplisht)
> Of their fair godlike young faces, a glory to compare
> With the immortal olive that circles bold Galileo's
> Brows, the laurel'd halo of Newton's unwithering fame ?

CHEMISTRY OF THE EARTH.*

By J. S. Anderson, Ph.D.

It is laid down in the terms of the Liversidge Lectureships that the lectures shall deal with new knowledge, and shall serve to promote research. Few developments in science have made so vital a contribution to chemical theory as has the knowledge that has been acquired, since Laue's discovery of the diffraction of X-rays, as to the constitution of the crystalline state of matter. This is especially true of inorganic chemistry, dealing, as it does, with compounds existing for the most part in the solid state as ionic or homopolar aggregates, rather than as molecular units. In this and the subsequent paper, therefore, the relation between crystalline structure and chemical theory will be taken as the general underlying theme.

The close association between chemistry and mineralogy obtaining in the early part of the last century is familiar to every chemist; nevertheless, with the passage of the years this association, so fruitful for the early growth of chemical theory, weakened, few chemists and geologists perceiving the fruitful fields of investigation that lay on the borders of the two sciences. Within recent years, however, and especially during the last two decades, there has been a greatly renewed interest in geochemistry—the chemistry of the earth—whereby the subject has been brought, in large measure, within the ordered domain of theoretical physical chemistry. This advance is due, in the main, to the work of a few schools of research—those of von Hevesy at Freiburg, I. and W. Noddack at Berlin, Clarke and Washington in America, and—above all—V. M. Goldschmidt at Göttingen and Oslo. The new subject so created, impinging on fields as diverse as nuclear physics, geology and metallurgical industry, appears eminently appropriate for a lecture which commemorates the work of Liversidge, who himself made so many contributions to Australian mineralogy.

The Data of Geochemistry.

The basic data of geochemistry are the analytical data of the world around us, the world of air and oceans and rocks immediately accessible to our investigation. Of this accessible world, by far the greatest mass is made up of the rocks of the *lithosphere*, represented by the exposed rock sections amounting to between 16 and 30 kilometres in aggregate thickness. About 95% of the lithosphere is composed of igneous rocks, with 4% of schists, 0·75% of sandstones, and 0·25% of limestones. Since, however, the materials of the sedimentary rocks must have been derived, in the first place, from the igneous rocks, as also was (for the greater part, at least) the solute of the oceans, it is clear that we may formulate as the first major task of geochemistry the establishment of the mean composition of the igneous rocks.

On this purely analytical question, finality has not yet been reached, in spite of the vast number of rock analyses that have been performed. Whereas there is substantial agreement as to the concentration of the major constituents of the lithosphere, such as are ordinarily determined directly in rock analyses,

* Liversidge Research Lecture delivered on October 27th, 1942, at Science House, Sydney, arranged by the Royal Society under the terms of the Liversidge bequest.

there have been far too few analyses in which those elements occurring only in minute amounts in igneous rocks have also been determined. The development of optical and X-ray methods of spectrochemical analysis has greatly extended the range of available data, and has led to a marked revision of the table of abundance of the elements. Much more work is needed, however, and some differences will be found between authoritative authors as to the abundance of the rarer elements in the lithosphere. Table I, based largely on the data of Washington and Clarke (1924), as revised by Noddack (1930, 1936*a*), sets out the present state of our knowledge.

Certain of the main features of Table I are familiar to most chemists, but there are a few points to which it is desirable to draw attention. There is, in the first place, the overwhelmingly predominant rôle played, in the lithosphere, by a small number of elements. About 99·5% of the entire mass of the igneous rocks is made up of twelve elements. Sixty-four out of the eighty-eight known elements together make up less than 0·04% of the total mass of the lithosphere.

Secondly, we may notice that some of the " common " elements that play the most important rôles in economic life, and that have been long known to and used by man, are actually comparatively rare. As examples one may cite copper, lead and antimony. Copper is less abundant than vanadium ; lead is comparable in abundance with thorium and molybdenum ; antimony is rarer that germanium or cæsium. Bismuth, mercury and gold are less abundant than any of the platinum metals. Although familiar to every student of chemistry, they rank in actual fact amongst the very rarest constituents of the lithosphere.

Complementary to the point just discussed is the abundance of certain elements far less familiar to most chemists—elements discussed in text books under the heading of the rarer elements. Most notable is the great importance of titanium in the composition of igneous rocks. Similarly, zirconium and vanadium are commoner than any of the heavy metals of commerce, other than iron, while the rare earths, taken as a group, are about as abundant as copper.

Consideration of these matters leads us to the conclusion that we must draw a clear distinction between the *abundance* of the elements and their *accessibility*. The elements that have been longest known, and that are most familiar to the student of chemistry, are those that occur in Nature as the major constituents of easily recognised minerals. We may distinguish between the *mineral occurrence* of elements and their *disperse occurrence*, and may trace a gradation in the measure of their dispersion in the earth's crust and in their accessibility. At the head of the list stands the occurrence of the elements in ore bodies—i.e., as major constituents of minerals which, through the mode of their formation, or through secondary processes, have been segregated in masses large enough for economically practicable working. Instead of being so segregated, however, many minerals are systematically dispersed as crystalline constituents of the rocks. This may be strikingly exemplified by the occurrence of titanium. Rutile, ilmenite, sphene, etc., are amongst the most widely spread of minor rock-forming minerals. Generally, however, it is only where these heavy minerals have been left as a mechanically resistant residue from the weathering and elutriation of rock masses that—as in our own valuable beach sand deposits of the New South Wales coast—we find titanium minerals segregated in considerable masses.

So far we have considered the occurrence of an element in its own crystalline minerals. Experience shows, however, that absolutely homogeneous crystalline minerals are of rare occurrence. They grew in nature from complex mixtures, and it is the rule, rather than the exception, to find in mineral crystals inclusions of foreign minerals, ranging in size from visible or microscopic crystals to regions on the microscopic verge of colloidal dimensions. In this connection, the

TABLE I.

Relative Abundance of the Elements.

(Composition of the earth's crust, including the oceans and the atmosphere, in percentage by weight.)

1. Oxygen	49,5 %			49. Praseodymium	$3{,}5 \cdot 10^{-4}$ %		
2. Silicon	25,7 „			50. Argon	$3{,}5 \cdot 10^{-4}$ „		
3. Aluminium	7,5 „			51. Cassiopeium	$1 \cdot 10^{-4}$ „		
4. Iron	4,7 „			52. Germanium	$1 \cdot 10^{-4}$ „		
5. Calcium	3,39 „						
6. Sodium	2,63 „	99,51%		53. Selenium	$8 \cdot 10^{-5}$ %		
7. Potassium	2,40 „			54. Caesium	$7 \cdot 10^{-5}$ „		
8. Magnesium	1,93 „			55. Terbium	$7 \cdot 10^{-5}$ „		
9. Hydrogen	0,87 „			56. Holmium	$7 \cdot 10^{-5}$ „		
10. Titanium	0,58 „			57. Thulium	$7 \cdot 10^{-5}$ „		
11. Chlorine	0,19 „			58. Niobium	$6 \cdot 10^{-5}$ „		
12. Phosphorus	0,12 „			59. Antimony	$3 \cdot 10^{-5}$ „		
				60. Uranium	$2 \cdot 10^{-5}$ „		
13. Manganese	0,09 %			61. Tantalum	$2 \cdot 10^{-5}$ „		
14. Carbon	0,08 „			62. Gallium	$2 \cdot 10^{-5}$ „		
15. Sulphur	0,06 „			63. Europium	$1{,}4 \cdot 10^{-5}$ „		
16. Barium	0,04 „			64. Indium	$1 \cdot 10^{-5}$ „		
17. Chromium	0,033 „			65. Thallium	$1 \cdot 10^{-5}$ „		
18. Nitrogen	0,030 „	0,45%		66. Cadmium	$1 \cdot 10^{-5}$ „		
19. Fluorine	0,027 „			67. Illinium	$< 1 \cdot 10^{-5}$ „		
20. Zirconium	0,023 „						
21. Zinc	0,02 „			68. Iodine	$7 \cdot 10^{-6}$ %		
22. Nickel	0,018 „			69. Platinum	ca. $5 \cdot 10^{-6}$ „		
23. Strontium	0,017 „			70. Palladium	ca. $5 \cdot 10^{-6}$ „		
24. Vanadium	0,016 „			71. Osmium	ca. $5 \cdot 10^{-6}$ „		
				72. Ruthenium	ca. $5 \cdot 10^{-6}$ „		
25. Copper	0,010 %			73. Silver	$4 \cdot 10^{-6}$ „		
26. Yttrium	0,007 „			74. Bismuth	$3 \cdot 10^{-6}$ „		
27. Tungsten	0,005 „			75. Mercury	$3 \cdot 10^{-6}$ „		
28. Lithium	0,004 „			76. Iridium	ca. $1 \cdot 10^{-6}$ „		
29. Rubidium	0,0033 „			77. Rhodium	ca. $1 \cdot 10^{-6}$ „		
30. Hafnium	0,0025 „	0,04%		78. Tellurium	ca. $1 \cdot 10^{-6}$ „		
31. Cerium	0,0022 „						
32. Lead	0,002 „			79. Helium	$8 \cdot 10^{-7}$ „		
33. Thorium	0,002 „			80. Neon	$5 \cdot 10^{-7}$ „		
34. Neodymium	0,0012 „			81. Gold	$1{,}5 \cdot 10^{-7}$ „		
35. Cobalt	0,0012 „			82. Masurium	ca. $1 \cdot 10^{-7}$ „		
36. Boron	0,001 „			83. Rhenium	ca. $1 \cdot 10^{-7}$ „		
37. Molybdenum	$7{,}5 \cdot 10^{-4}$ %			84. Krypton	$1{,}9 \cdot 10^{-8}$ %		
38. Bromine	$6 \cdot 10^{-4}$ „						
39. Tin	$6 \cdot 10^{-4}$ „			85. Xenon	$2{,}9 \cdot 10^{-9}$ %		
40. Scandium	$6 \cdot 10^{-4}$ „						
41. Beryllium	$5 \cdot 10^{-4}$ „			86. Radium	$7 \cdot 10^{-12}$ %		
42. Lanthanum	$5 \cdot 10^{-4}$ „			87. Protactinium	$2{,}6 \cdot 10^{-12}$ „		
43. Samarium	$5 \cdot 10^{-4}$ „						
44. Gadolinium	$5 \cdot 10^{-4}$ „			88. Actinium	$2{,}3 \cdot 10^{-14}$ %		
45. Dysprosium	$5 \cdot 10^{-4}$ „						
46. Ytterbium	$5 \cdot 10^{-4}$ „			89. Polonium	$1{,}4 \cdot 10^{-15}$ %		
47. Arsenic	$4{,}5 \cdot 10^{-4}$ „						
48. Erbium	$4 \cdot 10^{-4}$ „			90. Niton	$4 \cdot 10^{-17}$ %		

application of the electron microscope, with its great resolving power, to mineragraphic problems, holds promise of interesting information as to the gradation between such colloidal dispersions of one mineral in another and the atomic dispersion of the elements. This latter represents the ultimate degree of dispersion—the inclusion of foreign atoms, by isomorphous replacement, within the crystal lattice of the host.

Between these degrees of dispersion in the earth there is no sharp division. Every stage from the high grade ore to the atomic dispersion is represented in nature. One consequence—of philosophical rather than practical importance, perhaps—is the difficulty caused thereby in defining what is meant by a " pure mineral species ". No mineral analyses to an ideally simple formula, and even the diamond leaves a trace of ash when it is burned.

The Omnipresence of the Chemical Elements.

The foregoing considerations have been further developed by I. and W. Noddack (1936*b*) into an interesting, if controversial, hypothesis. Very few analyses of minerals have been made without any preconceived assumption as to the number of elements present. When such analyses are made, the results are somewhat surprising ; they show clearly that the range of elements detected depends solely on the limits of analytical sensitivity. Such an analysis of a zinc blende, reported by Noddack, is reproduced in Table II.

Table II.

Analysis of a Zinc Blende.

I	II	III	IV
Zn =63,55%	H =0,09%	Co, Ni, Cr, Mo, Ge, Sn, Ag, Hg, V, Te, Ga, In, Zr, Sr — each 0,01—0,001%	ΣY, La—Cp=0,00004%
S =31,92%	Ca =0,08%		ΣPlatinum metals=0,0007 %
O = 1,15%	Cd =0,08%		Re=0,00001%
Fe = 1,57%	Al =0,05%		
Si = 0,34%	Mg=0,04%		
Mn= 0,27%	Se =0,04%		
Pb = 0,15%	Cl =0,03%		
As = 0,14%	Sb =0,03%		
Cu = 0,13%	C =0,02%		
	P =0,02%		
	Na=0,01%		
	K =0,01%		
	Ti =0,01%		
	Bi =0,01%		
		Sc, W, Au, Hf, Th, U, Ba, Tl, Br — each 0,001—0,0001%	

In this table, column I records the major and column II the minor constituents determined by the ordinary methods of analysis. In column III are the constituents determined by optical or X-ray spectroscopy, either directly or after suitable chemical enrichment processes. In column IV are certain elements made the subject of special search by highly sensitive enrichment methods. Taking into account that the detection of any of the rare earths or the platinum metals connotes the presence of the whole group, and that the presence of uranium implies the presence of all its disintegration products, it will be seen that 75 elements were detected directly or indirectly in this sample. The only elements not found, in fact, were those for which a sufficiently sensitive analytical technique is lacking. The conclusion drawn by the Noddacks (1936*b*) from such results as these is that every " pure " mineral contains every element. Whether, as these authors consider, the conclusion can be extended to " pure " chemicals depends on the quantitative efficiency of chemical separation processes.

Their extensive work on the geochemistry of rhenium (Noddack, 1931) gave I. and W. Noddack the opportunity to amass a considerable body of data on the minor constituents of minerals, and this they have treated statistically from the standpoint of the omnipresence of the elements. There are, according to these authors, about 1,800 distinct mineral species known. If, for each element, there is plotted a distribution curve, showing the number of minerals containing more than 1%, 0·1%, 0·01%, etc., of that element, the curves so obtained have a similar form for all the elements. (Fig. 1.) Two points on the

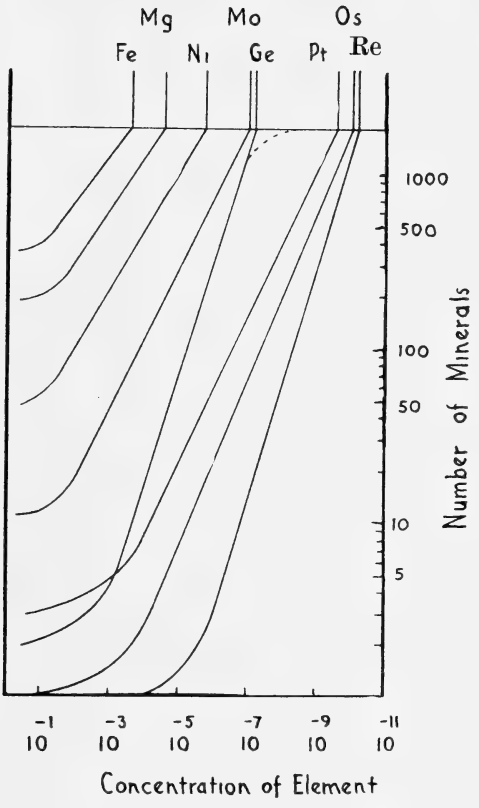

Fig. 1.—Statistics of distribution of elements in minerals.

curves have particular significance: (*a*) the point of inflexion, marking the concentration below which the disperse occurrence of any element is observed; and (*b*) the intersection of the curve with the ordinate at N = 1800, which represents the probable minimum concentration of that element in any mineral. For example, it is said that there are 360 minerals rich in iron, 700 with more than 1%, 1,250 with more than 0·1%. For molybdenum, a relatively rare element, there are 11 molybdenum minerals proper, with 25–70% Mo, 6 minerals with 1-3%, and (by inference from the 600 mineral species actually examined for molybdenum), 30 with 0·1-1%, 80 with 0·01-0·1%, 180 with 0·001-0·01%, 400 with 0·0001-0·001%. The Noddacks' figures are open to criticism on a number of counts; thus, the concentration of any trace constituent in any one mineral taken from different sources varies over a very wide range, so that mean values have little significance. For example, the indium content of zinc blende

varies from 0·1% to less than 0·0001%. Nevertheless, the general concept is worth some attention, and the idea of the "omnipresent concentration" of the elements in minerals has some meaning. The complementary idea is that of the probability of occurrence of any element above a certain concentration. For example, from the data given above regarding the concentration of iron in minerals, there is a probability of about 0·7 that any mineral taken at random will contain at least 0·1% of iron.

A further point brought out by the Noddacks' statistical treatment is that the number of minerals formed by any element is roughly a function of its abundance. $M = k \cdot A^x$, where M is the number of minerals formed, A is the abundance of the element, and the exponent x has about the same value (0·3-0·5) for all the elements (Noddack, 1936*a*). This relation is not absolutely rigid; if it were, one would expect that elements rarer than, say, antimony (Table I) would form no minerals of their own at all. This is not true, for the formation of compounds out of the originally uniform planetary matter must have depended on the chemical individuality of the elements, as well as on random fluctuations of composition of the mass. Thus, elements as rare as mercury and the platinum metals form their own characteristic minerals (native metals, sulphides, etc.), in virtue of their chemical inertness, affinity for sulphur, etc. On the other hand, rhenium and indium form no minerals of their own, and seem never to enter into the minerals of other elements to the extent of more than 0·01% and 1% respectively.

The chemical individuality of the elements, in so far as it conditions their mode of occurrence, can be measured by the ratio of their omnipresent concentration to their terrestrial abundance. This ratio, for a few elements, is listed in Table III. It is clear that elements prone to mineral formation—e.g., silicon,

Table III.

Element.	Omnipresent Concentration.	Lithosphere Abundance.	Lithosphere Abundance. / Omnipresent Concn.
Fe	$2{,}5 \cdot 10^{-4}$	$1{,}50 \cdot 10^{-2}$	60
O	$2{,}0 \cdot 10^{-4}$	$5{,}49 \cdot 10^{-1}$	2745
Mg	$2{,}7 \cdot 10^{-5}$	$1{,}42 \cdot 10^{-2}$	526
Si	$6{,}5 \cdot 10^{-5}$	$1{,}63 \cdot 10^{-1}$	2500
Al	$1{,}5 \cdot 10^{-5}$	$4{,}96 \cdot 10^{-2}$	3300
Ni	$1{,}7 \cdot 10^{-6}$	$6{,}47 \cdot 10^{-5}$	3·8
Mo	$1{,}0 \cdot 10^{-7}$	$5{,}77 \cdot 10^{-7}$	5·8
Ge	$6{,}6 \cdot 10^{-8}$	$2{,}46 \cdot 10^{-7}$	3·7
Sn	$1{,}5 \cdot 10^{-8}$	$9{,}01 \cdot 10^{-7}$	61
In..	$8{,}0 \cdot 10^{-9}$	$1{,}61 \cdot 10^{-8}$	2
Pt	$2{,}8 \cdot 10^{-10}$	$2{,}66 \cdot 10^{-9}$	9·5
Os	$1{,}0 \cdot 10^{-10}$	$1{,}24 \cdot 10^{-9}$	12·4
Re	$7{,}0 \cdot 10^{-11}$	$9{,}34 \cdot 10^{-11}$	1·3

oxygen, magnesium—occur almost exclusively in that manner, and are impoverished as regards their disperse occurrence. With increasing rarity, the ratio must necessarily diminish, and for an element that was uniformly dispersed it would reach the value unity. Rhenium comes very close to this, and other rare elements, such as indium and germanium, may be seen also to be comparatively uniformly distributed throughout the material of the earth's crust.

The foregoing considerations are not simply of academic interest. They are directly relevant to the problem of isolating the elements from natural sources. This is true even of the "common" elements; the amount of any

metal contained in the total ore deposits of the world is exceeded, by a vast factor, by the amount dispersed less accessibly through the rocks of the lithosphere. The problem of extracting aluminium is an obvious illustration. In felspars and clay minerals aluminium is widely and abundantly spread, but the segregation of aluminium in simple ores (i.e. high grade bauxite) is comparatively rare. Development of technically practicable methods of extracting aluminium from clay minerals is an urgent problem of the present day. Analogous problems relating to the other technically important metals will certainly confront the chemist of the future.

For the rare elements the matter is especially important, since these may, in many cases, be recovered solely, or at least most readily, as by-products of the extraction of base metals. The minute concentrations of rare elements in base metal ores (cf. Table II) are compensated by the large scale of metallurgical operations, whence suitably enriched products may be obtained from which to extract the rare constituents. A few examples may be cited to illustrate the realisation and the possibilities of such sources of rare elements. Thus, about half the world's platinum output is obtained as a by-product of the extraction of nickel from the Sudbury ore, which contains one part of platinum in two or three million of ore. Equally striking is the production of rhenium at low cost (Feit, 1930). The ultimate source of this has not been made clear, but it is probably the Mansfeld copper schist, which contains only about $4 \times 10^{-5}\%$ Re. The residues from which rhenium is extracted are themselves by-products of the recovery of molybdenum, which itself is present only to the extent of $0 \cdot 08\%$ in the original ore. Undeveloped potentialities are numerous. Sir Gilbert Morgan (1937 ; cf. Goldschmidt, 1935) has pointed out that, in consequence of the occurrence of gallium and germanium in significant amounts in the ash of British coals, upwards of a thousand tons of each of these rare elements are probably lost annually in smoke and flue dusts. Nearer home, we may cite the case of indium, which has recently attained a certain economic importance. The zinc blende and galena of Broken Hill both contain small but detectable amounts of indium, as recent Melbourne investigations have shown. The concentration in the ore is minute, but the quantities of material involved are such that, on a conservative estimate, about a ton of indium must pass through the flowsheets of the zinc and lead extraction plants each year.

The Absolute Abundance of the Elements.

The determination of the absolute abundance of the elements in the universe may be taken as one of the primary objectives of geochemistry, because the proportions in which the various species of atoms have been formed are presumably a measure of their relative nuclear stability. In so far as the data for the lithosphere are relevant, they show evidence of a regular periodicity to which attention was first drawn by Harkins ; namely, that elements with odd atomic numbers tend to be less abundant than those of even atomic number.

We cannot, however, assume that the rocks of the lithosphere are a representative sample of cosmic matter. In fact, such an assumption would be at variance both with the data of geophysics, as will be considered later, and with analyses of extraterrestrial matter, such as meteorites. The latter, and spectrographic evidence as to the composition of the sun, would lead beyond the bounds of the present discussion. We may note, however, that the mean composition of meteorites (Noddack, 1930 ; Hevesy, 1932) differs from that of the lithosphere in such a way as to accord more closely with Harkins' rule.

All the evidence points to the conclusion that the composition of the lithosphere differs from that of the earth as a whole. This being so, any relationship between the relative abundance of elements can be strictly valid only for groups of elements so alike chemically that they will not have been separated in any

physico-chemical process of differentiation. The rare earths provide an excellent illustration of such a coherent group (Fig. 2); their relative proportions are practically the same in the lithosphere, in meteorites, and in the sun (Noddack, 1935). It is worth noting that these data refer to the whole elements; between the abundance ratios for each isotope individually, the regularities are far more obscure. Harkins' rule owes its validity, in part, to the fact that, whereas elements of odd atomic number have only one isotope (or at most two), multiplicity of isotopes is common amongst elements of even atomic number.

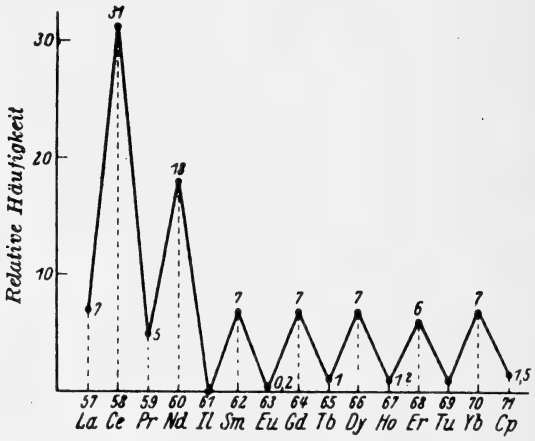

Fig. 2.—Relative abundance of rare earth elements.

In considering the relation between abundance and nuclear stability, it is fitting to touch briefly on the problem of the missing elements. In spite of the claims that have been made, it is fairly clear that four elements still remain to be isolated—those of atomic numbers 43, 61, 85 and 87. The entries for 43 (masurium) and 61 (illinium) in Table I should therefore be deleted. It will be noted, in the first place, that all are "odd" elements. Elements 85 and 87, from their position in the Periodic Classification, are unlikely to possess any non-radioactive isotopes, and may well be elements of short life. They do not belong to any of the three main disintegration series, so that if they now exist at all they must be derived from some improbable branching process or a rare isotope of the long lived radio elements. Practically, then, only ekamanganese (Noddack's masurium) and the rare earth metal (Smith-Hopkins' illinium and Rolla's florentium) remain to be isolated. What are the prospects for their discovery?

The study of isotope statistics has revealed a number of regularities which, although only empirical rules, do nevertheless accord with all the known elements. Mattauch (1934) has pointed out (*a*) that every element has at least one "odd" isotope; (*b*) that elements with odd atomic numbers are limited to nuclei with odd atomic weights; and (*c*) that of two isobares differing only by one unit of nuclear charge, one is invariably unstable—as, for example, the β-active ^{87}Rb, isobaric with ^{87}Sr. Isotope data for the known elements adjacent to elements 43 and 61 are set out in Tables IV and V. In each case, as was pointed out by Jensen (1937), all the likely nuclei are already represented among the stable isotopes of known elements. Thus ^{95}Mo, ^{97}Mo, ^{99}Ru, ^{101}Ru block the most probable nuclei for element 43, as do ^{143}Nd, ^{145}Nd, ^{147}Sm, ^{149}Nd and ^{149}Sm those likely for No. 61. Unless the atomic weights of these elements are abnormal, they come within the scope of Mattauch's rule, which would suggest that they

must be very rare, that they may be radioactive, and that they may, in fact, not exist.

Table IV.

Mass Number.	Z=36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43	44 Ru	45 Rh	46 Pd
84 ..	57	—	0·5	—	—	—	—	—	—	—	—
85 ..	—	73	—	—	—	—	—	—	—	—	—
86 ..	17	—	10	—	—	—	—	—	—	—	—
87 ..	—	27	7·5	—	—	—	—	—	—	—	—
88 ..	—	—	82	—	—	—	—	—	—	—	—
89 ..	—	—	—	100	—	—	—	—	—	—	—
90 ..	—	—	—	—	48	—	—	—	—	—	—
91 ..	—	—	—	—	11·5	—	—	—	—	—	—
92 ..	—	—	—	—	22	—	14	—	—	—	—
93 ..	—	—	—	—	—	100	—	—	—	—	—
94 ..	—	—	—	—	17	—	10	—	—	—	—
95 ..	—	—	—	—	—	—	15·5	—	—	—	—
96 ..	—	—	—	—	1·5	—	18	—	5	—	—
97 ..	—	—	—	—	—	—	10	—	—	—	—
98 ..	—	—	—	—	—	—	23	—	?	—	—
99 ..	—	—	—	—	—	—	—	—	12	—	—
100 ..	—	—	—	—	—	—	10	—	14	—	—
101 ..	—	—	—	—	—	—	—	—	30	0·1	—
102 ..	—	—	—	—	—	—	—	—	22	—	1
103 ..	—	—	—	—	—	—	—	—	—	99·9	—
104 ..	—	—	—	—	—	—	—	—	17	—	9
105 ..	—	—	—	—	—	—	—	—	—	—	23

Table V.

Mass Number	Z= 58 Ce	59 Pr	60 Nd	61	62 Sm	63 Eu	64 Gd
140 ..	89	—	—	—	—	—	—
141 ..	—	100	—	—	—	—	—
142 ..	11	—	36	—	—	—	—
143 ..	—	—	11	—	—	—	—
144 ..	—	—	30	—	3	—	—
145 ..	—	—	5	—	—	—	—
146 ..	—	—	18	—	—	—	—
147 ..	—	—	—	—	17	—	—
148 ..	—	—	1	—	14	—	—
149 ..	—	—	1	—	15	—	—
150 ..	—	—	—	—	5	—	—
151 ..	—	—	—	—	—	51	—
152 ..	—	—	—	—	26	—	—
153 ..	—	—	—	—	—	49	—
154 ..	—	—	—	—	20	—	—
155 ..	—	—	—	—	—	—	17

The Distribution of the Elements.

The second main problem of geochemistry concerns the distribution of the elements amongst the materials of the universe, and of our earth in particular. It has already been stated that the rocks of the lithosphere cannot be taken as representative of the whole earth, as simple geophysical considerations show.

In the first place, as Cavendish found, the mean density of the earth is about 5·8, whereas the density of the silicate rocks is about 2·6-2·8. Hence the interior of the earth must be composed of denser materials than the crust. Seismic evidence is in accord with this view, for the propagation of earthquake waves through the earth can be accounted for only if there are fairly abrupt discontinuities in the density and the elasticity of the earth at depths of 2,900 km. and 1,200 km. below the surface, as well as a less marked change at a depth of about 120 km. These discontinuities can only represent changes in material composition. What further evidence can be gained as to these materials of the earth's interior?

V. M. Goldschmidt, regarding meteorites as representative samples of planetary matter, has pointed out that in addition to the well known division into stony and iron meteorites, it is necessary to recognise a third meteoric material, troilite, which is associated with both iron and stony meteorites. Troilite is, predominantly, ferrous sulphide, together with other sulphides, such as daubréelite, $FeCr_2S_4$; upwards of thirty other elements have also been detected in minor amounts. The view may reasonably be advanced (Goldschmidt, 1922; Tammann, 1923, 1924) that the material of the earth initially underwent a similar separation into a four-phase system, consisting of a gaseous atmosphere and three immiscible liquid phases: a metallic liquid, consisting of a nickel-iron alloy by analogy with the siderites, a sulphide phase, mostly composed of ferrous sulphide, and a fused silicate phase. These, separating under the influence of gravity, would confer on the earth a structure (Fig. 3) compatible with all the geophysical evidence. In the meteorites, on account of the smallness of the masses involved, gravitational separation did not occur, so that the three phases, although very different in density, are frequently found intermingled physically.

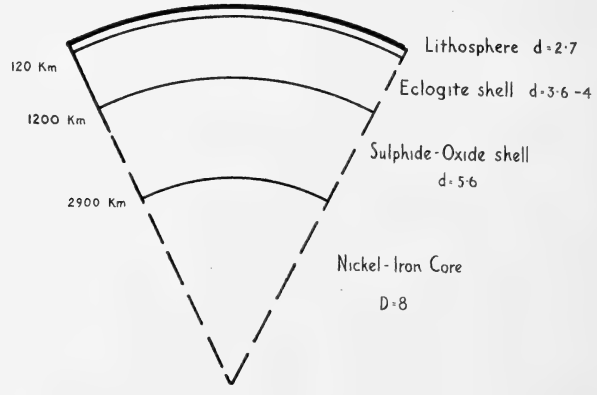

Fig. 3.—Section through the earth.

Evidence in support of Goldschmidt's view is found in the observation that just such a separation—into metal, matte and slag—is common in the metallurgy of sulphide ores, where it represents the phase equilibrium attained on the hearth of the furnace. In a three-liquid equilibrium of this kind there is a systematic distribution of the minor constituents between the phases, as was pointed out by Goldschmidt and Tammann (loc. cit.). For example, we have observed in Melbourne that in the lead blast furnace the trace of indium present is virtually absent from the silicate slag, and is strongly concentrated in the sulphide phase.

Laboratory experiments also show that the same separation of phases and partition of elements between them takes place in relatively simple mixtures,

as for example in a mixture of iron, ferrous sulphide and a fusible silicate. When solidification commences, a further differentiation occurs (cf. Paneth, 1925); a minor sulphide fraction separates from the silicate melt, owing to the decreasing miscibility of the liquids, while the initial, middle and final crystal fractions from the silicate phase differ systematically in composition.

From a study of the distribution of the minor constituents of a mixture in such laboratory experiments, in metallurgical processes, in meteorites, and in terrestrial minerals, the elements may be classified, following Goldschmidt, as *siderophile*, *chalcophile*, *lithophile* or *atmophile*, according as they are concentrated preferentially in the metallic, the sulphide, the silicate or the gaseous phase (Table VI). For example, nickel, gold and the platinum metals are enriched 1,000-5,000 fold in meteoric or native iron, as compared with the earth's crust. Other elements classed as siderophile display the same preferential concentration.

TABLE VI.

Goldschmidt's Classification of the Elements.

Iron, Siderophile.	Sulphide, Chalcophile.	Silicate, Lithophile.	Gases, Atmophile.	Organisms, Biophile.
Fe, Ni, Co	((O)), S, Se, Te	O, (S), (P), (H)	H, N, C, (O)	C, H, O, N, P
P, (As), C	Fe, Cr, (Ni), (Co)	Si, Ti, Zr, Hf, Th	Cl, Br, I	S, Cl, I (B)
Ru, Rh, Pd	Cu, Zn, Cd, Pb	(Sn)		(Ca, Mg, K, Na)
Os, Ir, Pt, Au *	Sn, Ge, Mo	F, Cl, Br, I	He, Ne, Ar	(V, Mn, Fe, Cu)
Ge,* Sn *	As, Sb, Bi	B, Al, (Ga), Sc, Y	Kr, X	
Mo, (W)	Ag, (Au), Hg	La, Ce, Pr, Nd, Sm		
(Nb), Ta	Pd, Ru, (Pt)	Eu, Gd, Tb, Dy		
(Se), (Te)	Ga, In, Tl	Ho, Er, Tu, Yb, Cp		
	(Cr)	Li, Na, K, Rb, Cs		
		Be, Mg, Ca, Sr, Ba		
		(Fe), V, Cr, Mn		
		((Ni)), ((Co)), Nb, Ta		
		W, U, ((C))		

* That germanium, tin, and gold are distinctly siderophile elements has recently been proved by independent studies on meteorites and on metallurgical products.

PHYSICO-CHEMICAL FACTORS UNDERLYING THE DISTRIBUTION.

In broad outline we can perceive the factors that determine the distribution of the elements in the kind of system under consideration. Iron, because of its preponderant abundance, is common to all the condensed phases—the metallic melt, rich in free electrons, the ionic silicate melt, and the semi-metallic sulphide melt, concerning the constitution of which we have as yet no satisfactory physical model. Elements higher in the electromotive series than iron must displace iron from the ionic melt, in which they are, accordingly, preferentially concentrated. The strongly electropositive elements are therefore *lithophile* in character. Conversely, the nobler metals are necessarily *siderophile*, being displaced by iron from the ionic liquid. The third main group, of *chalcophile* elements, contains those which form essentially homopolar compounds with the metalloids, and which cannot coexist in an ionic environment (melt or solution) with appreciable concentrations of metalloid ions. This group therefore comprises, in the main, the metals of the sulphide groups of analytical chemistry.

Whilst this qualitative treatment of the Goldschmidt classification is broadly correct, there are a number of outstanding problems regarding the magnitude of

the distribution coefficients. In fact, very few quantitative studies of this kind have been made. Jander (1925) measured the partition of gold between molten iron and fused silicates ; Noddack, Noddack and Bohnstedt (1940) that of gold, rhenium, molybdenum and the platinum metals between iron and ferrous sulphide. Jander and Rothschild (1928) examined equilibria between fused silicates and sulphides, and recently the author and Mr. M. J. Ridge have examined the distribution of several metals between the two coexisting liquid phases in the system tin-stannous sulphide. The general conclusions to be drawn from all these experiments are, firstly, that distribution is invariably more uniform than would be expected from simple thermodynamic calculation, and secondly, that the problem opens the whole question of the general theory of liquids. The chemistry and physics of fused salts and semi-metallic compounds is an outstanding field of fundamental research which impinges also on the province of the metallurgist. It would be a worthy object both for the research of the academic scientist and for the support and encouragmeent of the industrialist.

The Crystallisation of the Silicate Melt.

Our accessible world is derived from the crystallisation of the silicate phase, so that the geochemist is most closely concerned with the sequence of events in that process. With the onset of crystallisation, a process of differentiation must have commenced through the operation of gravitational forces. The first materials to crystallise from such a melt would be the heavy metallic oxides, such as magnetite and chromite, together with the denser silicates such as olivine, Mg_2SiO_4, and the magnesium metasilicate minerals (pyroxenes). All of these, we may note, are characterised by close-packed anion lattices, so that they represent the structures attaining the maximum density amongst silicates and oxides. Such minerals, settling through the melt, must have gone to build up the denser silicate-oxide shell of the earth. Included in this shell there are undoubtedly crystalline materials that could not be formed by crystallisation under ordinary pressures ; for example, the diamond, crystallised originally under enormous pressure, is brought to the earth's surface along with the typical silicate minerals referred to above.

The further course of crystallisation, as the temperature fell and the composition of the melt changed, can be correlated with the building of crystal lattices of increasing complexity of ordering, and higher lattice energy, the general sequence being :

orthosilicate unit —→ one-dimensional chains —→
lattices (pyroxenes)
two-dimensional —→ three-dimensional networks
sheet structures (aluminosilicates, felspars)
—→ three-dimensional openwork structures
(zeolites)

Distribution of Minor Elements During Fractionation.

To the free energy of formation of any solid ionic compound from its elements, factors of two kinds contribute. These are (*a*) those specific to the elements concerned—ionisation potentials, electron affinities, heats of sublimation and dissociation ; and (*b*) the cohesive energy or lattice energy of the compound, involving the structure and dimensions of the lattice unit. Where the thermodynamic quantities listed under (*a*) are known, the lattice energy may be derived by means of the Born-Haber cycle. Alternatively, following

Madelung, it may be calculated (for simple structures, at least) from the laws of force between ions

$$U_L = \frac{N.A.z^2.e^2}{R}\left(1 - \frac{1}{n}\right)$$

where A = Madelung constant.
z = valency of ions.
R = cell dimension.
n = repulsion exponent.

This expression for the Madelung energy* involves, as will be seen, the valency of the ions and the interionic distances in the lattice.

The sequence of crystallisation from a cooling melt follows, as was indicated above, the order of increasing lattice energy. It follows that, even between the major constituents of a complex melt, there must be a sorting process as crystallisation proceeds, according to the contribution of their ions to the cohesive energy of the solid phase.

The variation of cohesive energy with the ionic radius of the cation is typically exemplified by the orthosilicates of magnesium and iron:

Mg_2SiO_4	m.p. 1910°	radius	Mg_2^+	0·78 A.
Fe_2SiO_4	1205°		Fe_2^+	0·83 A.

Thus, magnesium has been concentrated preferentially in the earlier, and iron in the later crystallates from the magma. On the larger scale, magnesium must be relatively more abundant in the deeper silicate shell of the earth than in the lithosphere.

When we turn to the minor elements, present in atomic dispersion in minerals, we may infer that here again ionic radius has been one significant factor governing their distribution. The growth of our knowledge of chemical crystallography has shown that isomorphous replacement must be interpreted on a wider basis than is envisaged by Mitscherlich's law. Provided that an ion is metrically compatible with the lattice dimensions of a crystal, it may be able to replace another ion of different valency, the electrostatic balance between cationic and anionic charges being compensated either by another replacement elsewhere in the lattice, or else by the occurrence of one or more vacant lattice sites. This process, very clearly demonstrated by the chemistry of the silicates (cf. Bragg, 1937), we may conveniently term isomorphous replacement of the second kind. It follows that the mineralogical behaviour of the elements—i.e. their association with other elements and their rôle in mineral structures—is determined by their ionic radii rather than by their ordinary chemical characteristics, as is shown, for example, by the coordination numbers of the ions in oxide structures. (Table VII.)

From Table VII we may note how aluminium can replace, in silicate structures, either the silicon in 4-coordinate positions, or magnesium in 6-coordinate positions. Lithium, in virtue of its small ionic radius, necessarily replaces magnesium in 6-fold coordination, and cannot play the same part as do the other alkalis (coordination number 8). Titanium, similarly, must occupy 6-coordinate lattice positions, and cannot replace silicon, even though it is formally quadrivalent.

Although ions of different valency and slightly different size from those proper to a given lattice site can thus be incorporated in a growing crystal, it is evident that such isomorphous replacement will not be without effect on the cohesive energy. The sense of this effect may be seen from the expression given for the Madelung energy of the lattice. Hence, in the crystallisation of

* This term is convenient, since there are several correction terms, some not inconsiderable in magnitude, that must be taken into account in a rigorous computation of lattice energy.

TABLE VII.

Coordination Numbers of Ions in Oxide Structures.

Ion.	Radius Ratio.	Coordination Number.	
		Observed.	Predicted.
B^{3+}	0·20	3 and 4	3 or 4
Be^{2+}	0·25	4	4
Si^{4+}	0·38	4	4
Al^{3+}	0·41	4 and 6	4 or 6
Li^{+}	0·44	6	6
Mg^{2+}	0·47	6	6
Ti^{4+}	0·55	6	6
Na^{+}	0·56	6	6
Sc^{3+}	0·61	6	6
Zr^{4+}	0·63	6 and 8	6
K^{+}	0·76	8	8

Note.—These radius ratios are based on Pauling's univalent ionic radii; radii quoted in the text are effective, or Goldschmidt radii.

the earth's minerals from a complex melt there was a sorting action exercised on the basis of ionic radii and ionic charge of the minor constituents.

In the first place, amongst ions of the same valency, the smaller ions must have been taken up preferentially into the crystal. Larger ions, in consequence accumulated in the mother liquors. For this reason, rubidium, cæsium and thallium did not normally replace potassium in silicate minerals (ionic radii: K^{+}, 1·37Å.; Rb^{+}, 1·49Å.; Cs^{+}, 1·65A.; Tl^{+}, 1·49A.), and were ultimately concentrated almost exclusively in the minerals of the pegmatite dykes and other late crystal fractions. Conversely, where (as in the pairs nickel-magnesium, zirconium-hafnium) the ionic radii were very similar, little separation could arise during crystallisation. Thus, the magnesium-nickel ratio remained fairly uniform throughout all stages of crystallisation of silicate magmas.

The valency effect is even more significant than the ionic radius in determining the ease with which isomorphous replacement occurs. As between two ions of similar radius but different valency, the ion of higher valency is taken up preferentially in the earlier crystallate, that of lower valency accumulating in the mother liquors. The ions of scandium and lithium differ little in radius from the magnesium ion (radii: Sc^{+++}, 0·83Å.; Li^{+}, 0·78Å.). Scandium was therefore incorporated preferentially in place of magnesium in the early crystallates (e.g., early pyroxenes). We may logically infer that scandium is actually more abundant in the earth than analyses of the lithosphere suggest, most of the scandium having been taken up in the formation of the rocks of the deeper silicate shell. Lithium, on the other hand, replaces magnesium to an increasing extent in the later crystallates, as the following figures, taken from Goldschmidt (1937), show:

		Ratio $\frac{Li_2O}{MgO} \times 10^4$	
EARLY crystallates ..	Peridotite	0·12	
	Pyroxenite	0·17	
	Diorite	10	(upper limit)
LATE crystallates ..	Syenite	20	
	Nepheline syenite	70	
	Granite	600	

It is interesting to note, in passing, that the presence of all the rare alkalis in certain minerals, such as lepidolite, is accidental in that it arises from two causes. In the case cited, lithium has accumulated to replace magnesium because of its lower valency, while rubidium and cæsium have replaced potassium because of their larger ionic radii.

The figures just quoted show how our conclusions can be put to the test of experiment over a limited range amongst the materials of the lithosphere. On a much larger scale, the selective incorporation or rejection of minor elements between the deeper silicate shell and the lithosphere must have removed certain elements in large measure from our accessible world, while disproportionately increasing the concentration of others. Evidence that this has been done is obtained when we compare the abundance of the elements in the lithosphere and in stony meteorites which, for reasons mentioned earlier, are probably representative of the whole silicate phase. As Table VIII shows, elements that should have entered the early crystallates are, in fact, impoverished in the lithosphere, those that should have remained for the last crystallates are relatively enriched.

Table VIII.

Comparative Compositions of Lithosphere and Meteorites.

		Silicate Meteorites. (Concentrations in Grams per Ton.)	Lithosphere. (Concentrations in Grams per Ton.)	Ratio.
Early Crystallates	Cr	3,200	200	0·06
	Mg	137,000	21,000	0·15
Late Crystallates	Zr	80	190	2·3
	Na	3,700	21,400	5·8
	Li	5	65	13
	K	1,700	25,900	15
	Sr	20	420	21
	Ba	5	390	78

For the chemist, these data have interest as bearing on the question of the mutual association of the elements, and the sources from which rare elements may be obtained. It has been pointed out by various workers (Papish and Holt, 1930; Brewer and Baker, 1936) that the association of elements within the same horizontal period of the Periodic System is frequently more striking than that of elements of the same group—for example, the occurrence of every element from copper to selenium in zinc blende, and the customary association of indium with tin.

In the light of Noddack's arguments this loses some of its force, but it probably does reflect the systematic change in ionic radius which makes isomorphous replacement possible. Where, as in the transition series, a sequence of elements can display the same valency, with a very gradual decrease in ionic radius, the mutual association is particularly marked. The rare earths, of course, exemplify this very clearly.

The progressive rejection of certain elements by the growing solid phase must have led to their accumulation in the residual mother liquors of the magma. The elements concerned will have been those that cannot readily be built into ordinary silicate structures on account of their excessively small (e.g., B^{3+}) or excessively large ionic radius. In the latter category belong the rare alkalis, the rare earths, thorium, niobium, tantalum, tungsten and uranium. The

material of these mother liquors is found in the minerals of the pegmatite dykes, which have therefore become the collectors of rare elements in the lithosphere. It is proverbial that the typical minerals of these elements (e.g. samarskite, tantalite, uraninite) are extremely complex, and the local association of these minerals in a few regions, such as the Scandinavian mountains, is very striking.

In conclusion, we may notice that these elements, which we know only as very minor constituents of our world even after the gigantic enrichment experiment of the earth's solidification, must be truly rare in the cosmic sense. Among them, because derived from uranium and thorium, are the radioactive elements, so that the consequential phenomena of radioactivity—for example the development of heat within the earth's crust—must be largely concentrated within the lithosphere.

The subject of our consideration in this lecture lies, as was said at the outset, on the border of several sciences. Much of it, no doubt, belongs to the proper province of the geologist, and may bulk large in the geology of the future. Nevertheless, its recent rapid growth has come largely from the hands of the physical chemist. To both chemist and geologist, it sets old facts in a new light, and opens up vistas of problems not soon to be exhausted.

References.

Bragg, W. L., 1937. Atomic Structure of Minerals. Cornell Univ. Press, Ithaca.
Brewer, F. M., and Baker, E., 1936. *J. Chem. Soc.*, 1286.
Feit, W., 1930. *Z. angew. Chem.*, **43**, 459.
Goldschmidt, V. M., 1922. *Z. Elektrochem.*, **28**, 411.
Goldschmidt, V. M., 1935. *Ind. Eng. Chem.*, **27**, 1100.
Goldschmidt, V. M., 1937. *J. Chem. Soc.*, 654.
Hevesy, G., 1932. Chemical Analysis by X-rays. McGraw Hill, New York. Pp. 254 *et seq.*
Jander, W., 1925. *Z. anorg. allg. Chem.*, **143**, 377.
Jander, W., and Rothschild, E., 1928. *Z. anorg. allg. Chem.*, **172**, 129.
Morgan, G. T., and Davies, G. R., 1937. *Chem. and Ind.*, **15**, 717.
Noddack, I., and Noddack, W., 1930. *Naturwiss.*, **18**, 757.
Noddack, I., and Noddack, W., 1931*a*. *Z. physikal. Chem.*, **A, 154**, 207.
Noddack, I., and Noddack, W., 1931*b*. *Z. physikal. Chem., Bodenstein Festband*, 890.
Noddack, I., 1935. *Z. anorg. Chem.*, **225**, 337.
Noddack, I., 1936*a*. *Angew. Chem.*, **49**, 1.
Noddack, I., 1936*b*. *Angew. Chem.*, **49**, 835.
Noddack, I., Noddack, W., and Bohnstedt, J., 1940. *Z. anorg. allg. Chem.*, **244**, 252.
Paneth, F., 1925. *Naturwiss*, **13**, 805.
Papish, J., and Holt, D. A. *Z. anorg. allg. Chem.*, **192**, 90.
Tammann, G., 1923. *Z. anorg. allg. Chem.*, **131**, 96.
Tammann, G., 1924. *Z. anorg. allg. Chem.*, **134**, 269.
Washington and Clarke, F. W., 1924. *U.S. Geol. Survey*, Prof. Paper 127.

THE IMPERFECT CRYSTAL.*

J. S. Anderson, Ph.D.

In the formulation of our basic chemical theory, the study of gases and their generalised laws played, as every chemist and physicist recognises, a most significant part. During recent years we have acquired an entirely new insight into the constitution of the solid state of matter, which may well have a comparable effect in moulding our chemical outlook. This is especially true in the domain of inorganic chemistry, and the work of the Braggs and other pioneers in the field of crystal structure must be ranked, with Werner's theory, amongst the most important accessions to general chemical theory.

In any discussion of gases and their properties, we customarily draw a distinction between *ideal* gases and *real* or *imperfect* gases, recognising that the former, which obey the generalised gas laws and conform rigorously to Avogadro's hypothesis, are pure mental abstractions. For most purposes, of course, the conception of the ideal gas is sufficiently close in behaviour to the real gases with which we have to do experimentally. Nevertheless, the thermodynamic properties of real gases differ in certain directions from those of the hypothetical ideal gas, and the imperfections of real gases are responsible for some of their most important properties.

In the same way, our conventional concept of a crystal lattice is equally idealised, and represents also a pure mental abstraction. It is that of a crystal lattice in which every atom is situated on the appropriate lattice position, and every lattice position is occupied by the appropriate atom. It represents a compound of ideally stoichiometric formula, in true thermodynamic equilibrium at 0° K. As such it is, without doubt, quite unattainable in Nature. At any temperature above the absolute zero, all crystals must deviate to some degree from this " perfect " state ; *lattice defects* (German " Fehlordnungserscheinungen ") appear, and may be considered under two headings :

(*a*) Those that are inherent in the thermodynamics of the solid state, and

(*b*) those that are intrinsic to the particular crystalline compound under discussion.

As in the case of the imperfect gas, so these lattice imperfections underlie some of the most interesting physical and chemical properties of crystalline solids.

As is well known, we may broadly classify crystal lattices, according to the units of which they are composed and the forces binding them together, under the headings of metallic, homopolar-atomic, ionic and molecular crystals. In the first mentioned, the lattice points are occupied either by identical atoms (as in elementary metals) or by atoms that are electronically similar and usually interchangeable in function. These we shall not discuss, though order-disorder phenomena in alloys are not entirely unrelated to the subject of our consideration. Nor shall we deal with molecular crystals, although Ubbelohde and Oldham (1940) have described interesting investigations on the influence of known

* The second Liversidge Research Lecture, delivered on October 29th, 1942.

concentrations of lattice defects on the cohesive properties of molecular crystals. The remaining two lattice types represent limiting cases, towards one or other of which binary compounds tend in greater or lesser degree. The typical " homopolar " or " adamantine " compounds are to some extent heteropolar, being built up from elements of different electron affinity, while, as has been emphasised by Pauling (1939), there is a perceptible contribution of homopolar binding forces to the cohesion of the lattice even in compounds like the alkali halides. Between typical salts and homopolar compounds there is therefore a transition, rather than a sharp demarcation of lattice type.

We shall confine consideration, therefore, to heteropolar binary compounds, and treat the lattice imperfections displayed by them under the two heads already indicated. Firstly, then, we will consider lattice defects involving lattice disorder only, without infringement of the laws of stoichiometry, and secondly we will discuss those which give rise to crystalline phases of variable, non-stoichiometric composition.

Lattice Defects in Thermal Equilibrium.

If, in a stoichiometric crystal, any lattice site is left unoccupied, or if an atom be moved from its proper site to an interstitial position, a lattice defect is produced. Defects of the former kind—vacant lattice points (Fig. 1*b*)—are usually referred to as *Schottky* defects ; they necessarily originate in pairs (i.e., in equal numbers in cation and anion lattices respectively) in order to maintain the stoichiometric balance between anions and cations in the crystal as a whole. The other type, consisting of an interstitial atom together with the lattice site from which it came (Fig. 1*c*) is known as the *Frenkel* defect type. Its occurrence may be (and usually is) effectively limited to either cations or anions in the lattice.

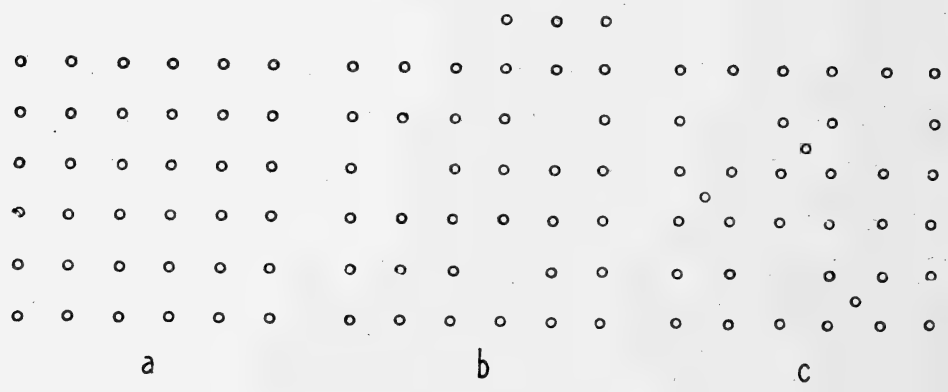

Fig. 1.—A simple point lattice (*a*), showing the development of Schottky defects (*b*), or Frenkel defects (*c*).

When such defects arise, the free energy of the crystal lattice is increased. The increase may be regarded as representing work done in removing an atom from an interior lattice site and placing it either at the surface of the crystal, to make a Schottky defect, or in an interstitial position within the lattice. Either process may arise from the thermal agitation of the atoms, but will necessarily affect only those atoms possessing not less than some critical energy. If the energy required to create a Schottky or a Frenkel defect be W_S, W_F respectively, the equilibrium concentration of lattice defects at any temperature T may be calculated quite simply, to a first approximation, by the methods of statistical

mechanics. If in a crystal of N lattice points, with N' interstitial positions, there are n lattice defects, then, to a first approximation,

$$n=(N-n)e^{-W_s/kT} \text{ for Schottky defects.}$$

$$n=\sqrt{(N.N')}e^{-W_F/2kT} \text{ for Frenkel defects.}$$

Both types of lattice imperfection are possible, and it is of interest to examine their relative importance in real crystals. It will be observed at once that the existence of lattice holes is common to both ; they differ, and consequently the relative magnitudes of W_s, W_F will also differ, with respect to the disposal of the atoms displaced in creating the hole.

Frenkel defects, from their nature, are likely to be important in crystals where the lattice structure is open enough to accommodate an atom in an interstitial position without much distortion. This is obviously possible in the zinc blende and wurtzite structures, for example, which are common to ZnO, ZnS, AgCl, AgBr, etc. Structures of closer packing and higher coordination number have little room for interstitial atoms. Further, where there is considerable disparity of size between anion and cation, it will clearly be easier to displace the smaller ion (usually the cation) to an inter-lattice position ; reference has already been made to the fact that Frenkel defects need affect only one of the lattice components. This is not necessarily the cation ; in the fluorite and related structures (e.g., CaF_2, CeO_2 ; also $PbCl_2$ structure) only the anion lattice, being of smaller coordination number, is markedly subject to Frenkel defects.

It follows that Schottky defects are intrinsically probable for cases not covered by the foregoing considerations, e.g. for the alkali halides and other compounds with the sodium chloride structure. As mentioned before, there will then be equal numbers of holes in both cation and anion lattices.

The lattice defects must be distributed statistically throughout the lattice, and so do not influence the symmetry of the crystal. They may, however, influence the lattice parameter, since they affect the lattice energy ; they may also make a perceptible contribution to such properties as the thermal expansion and the compressibility. Their greatest and most important effect, however, is upon the kinetic phenomena which may occur within the lattice, and which we will next consider.

Diffusion and Electrical Conduction within Crystals.

There are three obvious mechanisms whereby diffusion may take place in solids :

(*a*) Atoms or ions that are small in comparison with the interstices of the lattice may undergo the relatively free zeolitic diffusion. Apart from openwork lattices of the true zeolite type, capable of permeation by ions of fairly large radius, zeolitic diffusion applies also to the migration of small atoms (H, N, C, B) in metals with which they combine to form interstitial compounds. The diffusion of hydrogen in palladium, or of nitrogen in iron, is of this type.

(*b*) One can conceive of the cooperative synchronisation of thermal vibrations in a small zone of the crystal lattice, whereby an interchange of positions is made possible for a pair of adjacent ions in the centre of the zone. This mechanism has been discussed by Barrer (1941). It is not easy to assess the probability of such cooperative phenomena, but diffusion of this kind will clearly be relatively more important in the liquid state than in solids.

(*c*) Probably the most important mechanism in heteropolar crystals is by the migration of Schottky and Frenkel defects. An atom may move from an adjacent lattice site to a lattice hole or an interstitial atom may move from one inter-lattice position to the next (Fig. 2). In either case, the position of the lattice defect moves through the crystal, being associated with the movement of the atoms within the lattice.

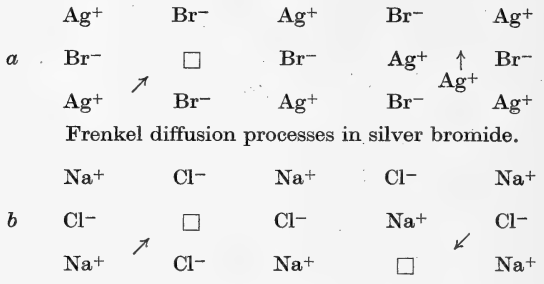

Fig. 2.—Diffusion of lattice defects.

The movement of an atom from an occupied lattice site to a neighbouring vacant site must involve the surmounting of a certain potential barrier. It is the height of this potential barrier that determines the activation energy for the diffusion process. Graphically, the energy changes during the process may be represented by Fig. 3, where the energy of the atom is represented as a function of its displacement from its equilibrium position in the lattice. Fig. 3*a* represents the activation energy for the migration of a Schottky hole ; Figs. 3*b* and 3*c* indicate respectively the movement of an atom between lattice site and interstitial position (creation or destruction of Frenkel hole) and the migration of an interstitial atom. It is generally considered that the activation energies for these two alternative Frenkel diffusion processes are likely to be about the same.

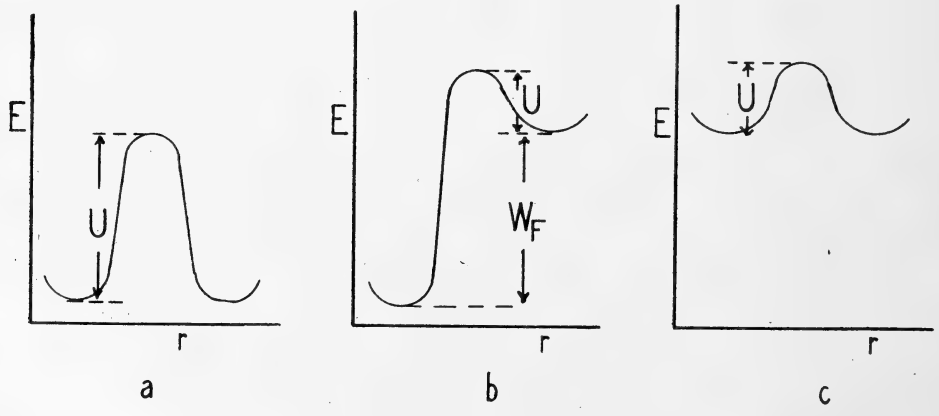

Fig. 3.—Activation energies for diffusion of lattice defects.

(*a*) Diffusion of Schottky defect.
(*b*) Creation or destruction of Frenkel defect.
(*c*) Migration of atom between interstitial positions.

The probability that a given lattice defect will be associated with the energy necessary to surmount the potential barrier U is, of course, proportional to $e^{-U/kT}$; the mobility is given as a function of temperature by

$$v = v_0 e^{-U/kT}.$$

Since the concentration of lattice defects is also an exponential function of the temperature, we have for the actual rate of diffusion

$$r = Ae^{-(E+U)/kT}$$

where A is a factor varying but little with temperature, and E is the energy for the production of a lattice defect ($=W_S$ or $\frac{1}{2}W_F$ as defined earlier). From the temperature coefficient of diffusion, the sum $(E+U)$ can be determined.

It is worth noting that in the Schottky mechanism it is, in effect, the hole that moves through the lattice, transporting with it a virtual charge of opposite sign to that of the ion properly occupying the lattice site in question. In sodium chloride, for instance, only the cations are mobile, except near the melting point. Diffusion takes place by the Schottky process (Figs. 2*b*, 3*a*), each mobile cation hole transporting a virtual negative charge.

Electrolytic Conduction in Crystals.

We have just seen how the existence of lattice defects connotes a certain possibility that they shall be mobile, in virtue of the thermal motion of ions within the crystal lattice. In the absence of any electrical field, the thermal movement of the ions is quite undirected, so that the position of the lattice defects will fluctuate at random. In an electric field, however, the movement of the ions in one or other field direction is favoured, depending on the sign of the mobile ions, so that the lattice defects will migrate along the electric field. By the movement of each defect an electric charge is carried through the lattice, so that the diffusion mechanism provides also a means for the transport of current through heteropolar crystals by an ionic mechanism.

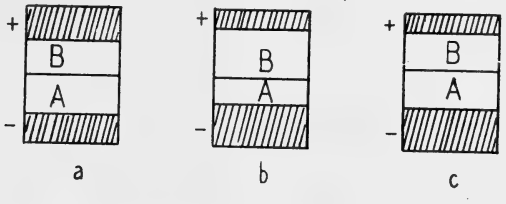

Fig. 4.—Transference experiment with solid electrolyte. (*a*) Initial state. (*b*) Final state, only anions mobile. (*c*) Final state, only cations mobile.

Although very poor conductors at the ordinary temperature, most salts show a marked increase of conductivity at elevated temperatures, as is implicit in the expression given for the dependence of diffusion upon temperature. It can be shown that the conduction of solid salts is electrolytic, and the relative mobilities of cations and anions can be determined, by the type of experiment represented diagrammatically in Fig. 4. Here (*a*) represents the initial state of the system, with two pellets of the salt (silver iodide, for example) clamped between electrodes of the appropriate metal (silver, in the instance cited). When a current is passed, the ions migrate through the pellets and are discharged at the electrodes. If the anions alone are mobile, the state after some time has elapsed will be represented by (*b*). Anions pass from pellet I to

pellet II ; at the cathode silver ions are discharged, at the anode silver is attacked. Hence pellet II increases in weight and pellet I decreases. If, as in (*c*), the cations alone are mobile, they pass right through the pellets from anode to cathode, and only the electrodes change in weight. In either case a complete balance sheet for the transference process may readily be constructed, whence, for salts in which both ions contribute to the conductivity (" bipolar conduction ") the transport number of each ion can be determined, the final state being then intermediate between (*b*) and (*c*).

Measurements involving this kind of technique have been made for many binary salts, especially by Tubandt and his co-workers (Tubandt, 1927, 1931, 1932, 1933 ; also Jost, 1937 ; Mott and Gurney, 1940 ; Seitz, 1940). The mechanism of conduction in salts has thereby been largely clarified. In the sodium and potassium halides just below the melting point, both ions are mobile. This, however, is exceptional. Only the cations are mobile in sodium chloride at lower temperatures, as also in the halides, sulphides, selenides and tellurides of copper and silver. The halides of barium and lead are pure anion conductors, due—as indicated previously—to the mobility of Frenkel defects in the anion lattices of these salts.

The Concentration of Lattice Defects in Thermal Equilibrium.

We have seen that kinetic processes—diffusion or electrical conduction—involve both the concentration of lattice defects and their mobility. Thus, if x be the concentration, and v the mobility of a Frenkel defect, in a lattice with N lattice points per unit volume, the electrical conductivity is given by

$$\sigma = N\mathbf{e}vx$$

or, substituting for v and x the values cited earlier,

$$\sigma = N\mathbf{e}v_0x_0e^{-(U+\frac{1}{2}W_F)/kT}.$$

The temperature coefficient of conductivity, therefore, like that of diffusion, affords a measure of $(U+\frac{1}{2}W_F)$; conductivity measurements are, in practice, the more convenient experimentally. Neither conductivity measurements nor diffusion measurements provide a means of measuring the actual concentration of lattice defects, however, without supplementary data to separate the two factors that contribute to the overall rate of the kinetic process.

Koch and Wagner (1937) have, by an ingenious device, overcome this difficulty by varying the concentration of lattice defects independently of their mobility, i.e. by varying the concentration of lattice defects at constant temperature. Silver chloride and bromide form mixed crystals with up to one per cent. of the corresponding cadmium and lead halides. In these, to preserve the stoichiometric balance between anions and cations, each Cd^{++} or Pb^{++} ion must replace two Ag^{+} ions, with the result that one cation site is left vacant for each Cd^{++} or Pb^{++} ion introduced. The concentration of permanent holes thus created is equal to the concentration of bivalent ions. At constant temperature, the conductivity is proportional to the total concentration of lattice defects, and since the addition of 1% of $CdCl_2$ to AgCl was found to increase the conductivity more than 100-fold, it is clear that the number of holes created artificially far outweighed the number present in thermal equilibrium. In such a mixed crystal, therefore, the temperature coefficient of conductivity must have measured only the increase in mobility of the lattice defects, without sensible increase in their concentration. The height of the potential barrier U was thus found directly, and by comparison with measurements on the pure silver halides, the concentration of interstitial silver ions in thermal equilibrium

in pure AgCl and AgBr can be calculated. By this means, the following data were obtained.

	AgCl.	AgBr.
Concentration of lattice defects ..	$x=36e^{-\frac{25000}{2kT}}$	$29e^{-\frac{20000}{2kT}}$
Mobility of lattice defects	$v=0\cdot12e^{-\frac{6000}{kT}}$	$0\cdot95e^{-\frac{8200}{kT}}$
Activation energy U, for diffusion ..	6,000 cals.	8,200 cals.

From these figures, the concentrations of thermal defects at a few temperatures are as follows :

AgCl	300° C.	$5\cdot5 \times 10^{-4}$
	210°	$8\cdot1 \times 10^{-5}$
AgBr.. ..	426°	$2\cdot0 \times 10^{-4}$
	300°	$4\cdot0 \times 10^{-3}$
	210°	$7\cdot6 \times 10^{-4}$
	20°	$8\cdot3 \times 10^{-6}$
	−180°	10^{-22}

From the theoretical relationship between conductivity and temperature, it is evident that the logarithm of the conductivity should be a linear function of $1/T$. This is the case experimentally, but it is usually found that a curve with two rectilinear limbs results. At high temperatures the conductivity is a highly reproducible property, and the slope of the curve measures $(U+E)$. At lower temperatures, the conductivity is reproducible neither from one specimen of a salt to another, nor even for the same specimen after varying heat treatment. It is said to be structure-sensitive, and reflects the operation of some process of lower activation energy. Whether this is surface diffusion in the surfaces of a Smekal mosaic structure of the crystals, or whether impurities influence the low temperature conduction mechanism (as was deliberately the case in Koch and Wagner's experiments) is a problem still open to debate.

There are a number of substances—Ag_2HgI_4, AgI, Ag_2S—which display a type of allotropy of particular interest to the crystallographer. In the high temperature modification of each of these (Ketelaar, 1938 ; Strock, 1934, 1936) it is found that the cations are distributed at random over a number of crystallographically equivalent positions. Interstitial positions and ideal positions are indistinguishable, so that the energy W_F is virtually zero, while the potential barrier U is not very high. The result is that such compounds have an astonishingly high conductivity.

It will have been noted that such experiments as those of Tubandt, referred to above, imply that ions may migrate freely across the interface between two samples of solid—whether single crystals or compressed polycrystalline pellets. This is indeed so, even for the interface between salts of different crystal structure and lattice spacing, provided that the mobile ion is common to both lattices. Thus, there is free transport of silver across the interface AgI | AgCl, or AgI | Ag_2S. It does not hold true, generally speaking, for foreign ions, except where ready solid solution occurs. An instance of the latter is provided by the observation that if a pellet of Ag_2S containing 1% of Cu_2S, and a pellet of Ag_2S be superposed, uniformity of composition is very rapidly established at 200-300°, by the migration of copper from one pellet to the other. As a rule, foreign ions are not accepted in appreciable amount by a crystal lattice. Gold may be introduced into sodium chloride crystals at 600° by electrolysis between gold electrodes. On cooling, however, the gold atoms aggregate together into particles of colloid dimensions. Nickel atoms may similarly be introduced by electrolysis between nickel electrodes, but not by ionic migration across the interface between sodium chloride and nickel salts.

Reactions in Solids.

We have, in the foregoing, direct evidence as to both the occurrence and the mechanism of that mobility of ions which is the necessary prerequisite for the occurrence of reactions in the solid phase.

The most fundamental contributions to this subject have probably been made by Wagner and his co-workers (1933, 1934, 1936*a*, 1936*b* ; cf. also Jost, 1937, chapter IV, for further extensive bibliography), who have rigorously established the relationship between (*a*) the reaction processes at the interface of a metal and a gaseous or liquid non-metal (" tarnish reactions ") and (*b*) the processes of diffusion and electrolytic conduction in the binary compound formed. Thus, in a system of superimposed pellets represented diagrammatically as

$$\mathrm{Ag} \mid \mathrm{Ag_2S\ I} \mid \mathrm{Ag_2S\ II} \mid \text{liquid S}$$

it is found that only pellet II grows in size, and this is explicable only in terms of the migration of Ag^+ ions through the system, and reaction at the Ag_2S–S interface. The evidence is complete that it is Ag^+ ions, not neutral Ag atoms that diffuse by the processes already considered, and it follows that there must be an independent compensating flow of electrons in the same direction. The phase boundary reaction is thus between electrons and sulphur, with formation of sulphide ions. There are three independent rate processes to be considered ; the rate of migration of cations, the rate of migration of electrons, and the velocity of the boundary reaction. It is the slowest of these (in this instance the migration of electrons) that determines the overall rate of chemical change.

Similar considerations apply to the oxidation of metals that form coherent oxide films (e.g., iron) and also to what may be termed (Wagner, 1936*b*) ionic reactions of higher order. The latter comprise reactions between binary compounds to form salts, double oxides, etc., as exemplified by the formation of spinels and similar compounds (Fig. 5) and by the reactions of silicates (Fig. 6) (Jander and co-workers, 1931*a*, 1931*b*, 1932, 1934, 1935 ; Hedvall, 1931 ; see also Jost, 1937, chapter V, for further bibliography).

	MgO	$MgO \cdot Al_2O_3$	Al_2O_3	
Ionic Diffusion		$3Mg^{++} \rightarrow$ $\leftarrow 2Al^{+++}$		(I)
Phase-boundary reaction	$4MgO$ $-3Mg^{++}$ $+2Al^{+++}$		$4Al_2O_3$ $-2Al^{+++}$ $+3Mg^{++}$	
	$=1MgO \cdot Al_2O_3$		$=3MgO \cdot Al_2O_3$	

Fig. 5.—Solid phase reaction—I. Spinel formation.

	MgO	Mg_2SiO_4	$MgSiO_3$	
Ionic Diffusion		$2Mg^{++} \rightarrow$ $\leftarrow Si^{++++}$		(II)
Phase-boundary reaction	$4MgO$ $-2Mg^{++}$ $+Si^{++++}$		$4MgSiO_3$ $-Si^{++++}$ $+ Mg^{++}$	
	$=Mg_2SiO_4$		$=3Mg_2SiO_4$	

Fig. 6.—Solid phase reaction—II. Typical silicate reaction.

It will be noticed that, in the ionic reactions of higher order, there is a counter flow of ions rather than the migration of free electrons ; also that, in these instances, the anions remain relatively immobile. In the processes of

Figs. 5 and 6, the oxygen atoms form a fairly close packed anion lattice both in the reactants and in the product. It is the relatively small and mobile cations that diffuse through the interstices of the anion lattice. Although our knowledge of reactions between solids has been greatly augmented by the work of W. Jander, Hedvall, Hüttig and others, there is still a paucity of data on the kinetics of the process, so that a quantitative comparison with our fairly precise theoretical picture is possible only in a few instances.

Non-stoichiometric Crystals.

In all that has been discussed hitherto, it has been assumed that lattice defects occur in balanced pairs ; that is, in Frenkel defects, an interstitial ion and a lattice hole (which represents a virtual charge of opposite sign), or in Schottky defects, equal numbers of holes in both cation and anion lattices. If the defects are not present in such pairs, the stoichiometric balance between the constituents of the compound is destroyed, and its formula is no longer uniquely determined.

A crystalline phase in which this state of affairs obtains is commonly stated to contain an excess of one or other constituent " in solid solution ". In the light of our knowledge of the constitution of the solid state we are able to attach to this expression a more precise significance than formerly. There are three possible types to which the " solid solution " of the element B in the compound AB can conform. In *substitutional* solid solutions, atoms of B occupy lattice sites that would normally be occupied by atoms of A. Clearly, this could not occur in ionic compounds, on electrostatic grounds, so that this type of solid solution is practically restricted to alloys and intermetallic compounds, where both elements are present in the lattice in a similar electronic state. *Interstitial* (or additive) solutions are, as the name implies, related to the development of Frenkel defects, atoms of B being present interstitially in the lattice of AB in greater concentration than the vacant B-atom sites. *Subtractive* solid solutions are similarly related to Schottky defects, the numbers of vacant A-atom and B-atom sites being unequal.

Consideration of the thermodynamic stability of such non-stoichiometric compounds will be deferred for the moment. It may, however, be noticed that to preserve electrostatic balance in the crystal, one or other constituent must be present in more than one valence state. This will be clear from Fig. 7, referred to below. According as the metal or the non-metallic constituent is present in excess, there are four possible ways in which non-stoichiometry may arise.

(*a*) Metal in excess.
  (i) Anion lattice complete, with metal atoms in interstitial positions.
  (ii) Anion lattice incomplete (i.e., vacant anion lattice sites), with perfect cation lattice.

(*b*) Non-metal in excess.
  (i) Cation lattice complete, with non-metal atoms interstitially.
  (ii) Cation lattice incomplete (vacant cation positions), anion lattice complete.

These possibilities are, of course, subject to ordinary thermal lattice defects, superimposed on the non-stoichiometry. There is general agreement that the types (*a*-i), based on unbalanced Frenkel defects, and (*b*-ii), based on unbalanced Schottky defects, represent the most important cases.

For an example of the application of these principles we may cite cuprous oxide. This, as is well known, has a range of composition on the oxygen-rich side of the formula Cu_2O, and the constitution of the non-stoichiometric phase

may be illustrated diagrammatically by Fig. 7. For every O^{2-} ion in excess of the stoichiometric balance, two Cu^{+} ions must be replaced by two Cu^{2+} ions, and two Cu^{+} lattice sites must be left vacant.

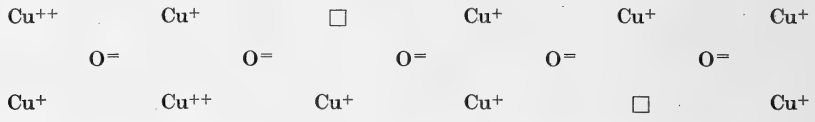

Fig. 7.—Lattice defects in cuprous oxide with excess oxygen (=deficit of copper). Vacant cation sites marked by squares.

Electrical Conductivity of Non-stoichiometric Compounds.

As with thermal lattice defects in ionic compounds, so the electrical conductivity of non-stoichiometric compounds provides a phenomenally sensitive and very instructive means of studying their properties. Here, however, electronic (i.e. metallic) conduction, not electrolytic conduction, is involved.

In discussing the electronic constitution of heteropolar compounds, we may use either of two approximations, which correspond respectively to the Heitler-London and the Hund-Mulliken approaches to the problem of molecular structure. Either is permissible, but they are not necessarily equally useful as descriptions of any particular structure. The *discrete ion* picture represents the only interaction between ions as due to the electrostatic attraction or repulsion of their net charge : the electronic levels within any ion are assumed to be unaffected by the proximity of contiguous ions. This model gives a very fair approximation for crystals built up from inert gas-like ions (e.g., NaCl, CaF_2) in their ground state. It implies that the energy of excitation of an electron to the continuum of levels is practically the same as the ionisation energy of the isolated ions. Alternatively, the *collective electron*, or *band* approximation regards the electrons as moving in the periodic field of all the atoms of the crystal. It affords the most useful description of semi-metallic compounds, in which the polarisation effect of cation and anion is very large. The same compounds tend to display electronic conductivity. Qualitatively, this model is not unfamiliar, for it has long been recognised (Grimm and Sommerfeld, 1926) that certain series of compounds, such as CuBr, ZnSe, GaAs, Ge itself, in which there are, in every case, eight valency electrons between the two atoms, crystallise in a common structural type with almost identical lattice dimensions : all eight valency electrons are utilised in bonding, irrespective of the formal valency of the atoms. In the collective electron model, the discrete electronic energy levels of the isolated atom are replaced by bands of permitted energies. Within any one band, and subject to the Pauli principle, the energy of an electron may change continuously, but the excitation of an electron from one band to the next (corresponding to a quantum jump in an isolated atom) involves the expenditure of energy far in excess of thermal energies. On the model first advanced by Wilson (1931), the essential difference between insulators and electronic semi-conductors lies in the possibility of promoting electrons to an unoccupied energy band. In any electronic conductor, there can be a net flow of electrons only in an incompletely filled energy band, so that a crystal is an insulator if every energy band is either completely full or completely empty. The typical inorganic compounds are insulators in this sense, and the excitation of an electron to the lowest conduction band would demand a high energy of excitation. In a Wilson semi-conductor (intrinsic semi-conductor), the spacing between successive energy bands is such that electrons may be promoted to the conduction band by thermal energies. It is probable that no semi-metallic compound owes its conductivity at the ordinary temperature to this simple mechanism.

The formation of non-stoichiometric compounds is directly related to the development of electronic conductivity, however, since it provides a mechanism for the ready transfer of electrons from atom to atom through the lattice. For, consider the possibility of an electron switch from atom to atom along a row of identical cations—e.g., in nickel oxide, NiO, of stoichiometric composition. The process [A]→[B] (Fig. 8) is inherently improbable, and must be followed by a reversal of that process, rather than by the propagation of the perturbation along the lattice row. However, in black nickel oxide, of composition $NiO_{1\cdot 005}$, for instance (cf. Klemm and Hass, 1934), five Ni atoms in every thousand are presumably present as trivalent ions. If, in a lattice row containing a Ni^{+++} cation, an electron switch takes place (Fig. 8, process [C]→[D]), we may see that the resulting state of the system is energetically indistinguishable from the original state.

$$Ni^{++}\quad \underset{[A]}{Ni^{++}}\quad Ni^{++}\quad Ni^{++} \longrightarrow Ni^{++}\quad \underset{[B]}{Ni^{+}}\quad Ni^{+++}\quad Ni^{++}$$

$$Ni^{++}\quad \underset{[C]}{Ni^{+++}}\quad Ni^{++}\quad Ni^{++} \longrightarrow Ni^{++}\quad \underset{[D]}{Ni^{++}}\quad Ni^{+++}\quad Ni^{++}$$

Fig. 8.

It follows from the general principles of quantum mechanics that the migration of electrons along a lattice row in this fashion is readily possible, being governed by the probability of leakage of an electron through the potential barrier between the dissimilar ions. When an electric field is applied, therefore, a mechanism exists for a drift of electrons, the conductivity being determined (*a*) by the magnitude of the potential barriers, and (*b*) by the number of " positive holes " in the conduction band. This latter, as will be noticed, is measured by the degree to which the compound departs from stoichiometric composition. We do not, for our present purpose, need to go further into the mechanism of conduction (cf. Mott and Gurney, 1940 ; Seitz, 1940).

As has been stated, intrinsic semi-conductors are almost or quite unknown : the energy gap between the full bands and the conduction band is relatively large in every case, for pure compounds. In every case that has been investigated, however, the electronic conductivity of compounds displaying semi-metallic properties is a function of the composition in exactly that manner according with the considerations we have set out.

Amongst the metallic oxides, which constitute the best investigated group of electronically conducting compounds, two main types of semi-conductor are recognised. In the first, exemplified by Cu_2O, FeO, CoO, NiO, etc., it is found that the conductivity increases as the partial pressure of oxygen in equilibrium with the solid is raised. This implies that these compounds have some range of composition on the oxygen-rich side of the ideal formula. If, at temperatures where reaction can occur, the partial pressure of oxygen is raised, a reaction takes place, which may be symbolised by

$$2M^{+}+\tfrac{1}{2}O_2 \longrightarrow O^{--}+2M^{++}+2\square.$$

The crystal lattice is thereby extended by the addition of a new anion lattice point, while new vacant cation lattice points, and new positive holes for conduction, are introduced in equivalent amount.

The second type of oxide semi-conductor is that in which the conductivity diminishes as the partial pressure of oxygen in the system is raised. In this case, combination with oxygen obviously destroys the defects upon which conduction depends. Zinc and cadmium oxides are of this type, and the formation of conducting centres by loss of oxygen from the crystal may be symbolised as

$$M^{++}+O^{--} \longrightarrow \tfrac{1}{2}O_2+M.$$

Anion and cation lattice points disappear in equal numbers, and are replaced by a corresponding number of interstitial metal atoms. Compounds of this kind have, then, a non-stoichiometric range of composition on the metal-rich side of the ideal formula.

The Thermodynamic Stability of Non-stoichiometric Compounds.

A complete theoretical treatment of the relation between the free energy and the composition of a non-stoichiometric compound is lacking as yet. Such a treatment must take account of a number of factors which, by their interplay, must underly the experimental fact that, in certain instances, the permissible range of composition is very considerable. These factors need not be enumerated here.

Schottky and Wagner (1930) have treated the problem from the formal thermodynamic standpoint. While their results cannot be explicitly evaluated, they are interesting as showing firstly, that the activity of each component in a crystalline phase is a continuous function of composition, and secondly, that the range of composition over which a non-stoichiometric phase exists is itself a function of the degree of lattice disorder that obtains. This implies that the composition range of any such compound should be wider at higher temperatures.

Related to the second point raised by Schottky and Wagner is the correlation that may be drawn between the type of non-stoichiometry exhibited by a compound, and the type of favoured lattice disorder. Thus, the wurtzite type lattice of zinc oxide is of a type favouring Frenkel defects in thermal equilibrium : in non-stoichiometric zinc oxide, the excess zinc is almost certainly present interstitially, due to the formation of unbalanced Frenkel defects as oxygen evaporates out of the lattice.

It has been pointed out by Mott and Gurney that whenever a polar compound is in contact with an excess of one or other component, the formation of a non-stoichiometric phase must ensue, even though the extent to which deviation from ideality occurs is immeasurably small. An illustration of this thesis where, on classical chemical ideas, it would not be expected, is found in the formation of blue crystals of sodium chloride when the salt is heated in sodium vapour. With this in mind, we may return to the problem of solid reactions, such as the " tarnish " reactions of Wagner. In the process of forming silver sulphide, considered previously, we now see that there must be a certain composition gradient through the solid, since one side is in contact with silver and the other side with sulphur. To the deviation from the ideal formula Ag_2S we may reasonably ascribe the liberation of mobile electrons necessary for the occurrence of the phase boundary reaction.

The range of compositions over which a compound can persist is one of the most interesting problems. In metal-excess systems, the stable range seems usually to be immeasurably narrow, and accessible to investigation only from measurements of the conductivity and the Hall effect (cf. Fritsch, 1935). When however, compounds are formed with an excess of non-metal, due to the potential variability in valency of the metallic constituent (e.g., Cu_2O, FeS), we may note two factors that can materially widen the range of stable composition. These are, firstly, that an increase in valency of a metallic cation makes a large contribution to the Madelung energy of the surrounding lattice points ; and secondly, that in consequence of the statistical distribution of higher-valent cations and lattice holes, there is a progressive and very marked change in the lattice parameter as the composition changes. This shrinkage of lattice spacing, as the non-metal excess increases, again reacts upon the cohesive energy of the lattice. In a qualitative way one can see how these two factors may balance out the endothermicity of lattice hole production over a certain range of composition. In exceptional cases (e.g. FeS, the tungsten bronzes) this range may be very

wide, and the experimental evidence leaves no doubt that the maximum of stability may actually differ from the stoichiometric ratio : stoichiometric FeO and FeS do not exist (Hägg, 1933, 1935 ; Jette and Foote, 1933 ; Bernal, 1933).

We may, in conclusion, examine how far the matters discussed are relevant to the familiar facts of chemistry. The formation and properties of metal-excess conductors are known to every student, for the colour change of zinc oxide from white to yellow when heated runs parallel to the development of electronic conductivity. The marked optical absorption in the visible region in itself marks the diminished energy of excitation of electrons from the ground level to the excited state. Where similar colour changes occur with other oxides (e.g., with indium oxide, and with more refractory oxides at higher temperatures), we may reasonably infer that the same process is operative, and that we are observing the evaporation of oxygen from the crystal lattice, and the formation of a non-stoichiometric phase. A wide variety of observations can be brought under the same general heading, including the properties of refractory oxides and ceramic masses at high temperatures.

Attention has already been drawn to the particular interest attaching to the non-metal excess compounds, and the apparent non-existence of the stoichiometric compounds in several familiar instances. The oxide and sulphide of univalent copper likewise extend as uniform phases at least up to the compositions $Cu_{1\cdot995}O$, $Cu_{1\cdot98}S$. It seems as if non-stoichiometric compounds are formed whenever the valence properties of the metal permit it, and as if the range of permissible composition becomes wider as the electronegativity of the non-metal diminishes.

In this connection, the highly coloured, metallic-looking sulphides of the heavy metals are of especial interest. Their optical properties, so different from those of the true salts of the same metals, suggest that amongst them might be found the intrinsic semi-conductors of Wilson's theory. They have hitherto received but little experimental investigation, however, in comparison with the oxides of the metals. According to recent work carried out in Melbourne, stannous sulphide and lead sulphide belong to the class of non-stoichiometric conductors, with a non-metal excess. Both metals, it will be noted, can potentially exert quadrivalency. The extraordinary sensitiveness of the electrical conductivity towards changes in composition is well illustrated by some of our results. Assuming a reasonable value for the mobility of an electron in stannous sulphide, it appears that " pure " stannous sulphide, as prepared by ourselves and other authors according to a standard procedure, contains about 2×10^{18} conducting centres per gram-molecule. This is due to excess of sulphur, and the upper limit of composition corresponds to the formula $SnS_{1\cdot00001}$. By suitable treatment with hydrogen, the excess of sulphur is partially removed : positive holes are thereby destroyed, and the specific resistance is raised more than one thousandfold, corresponding, perhaps, to a composition $SnS_{1\cdot00000001}$. As this work will be described elsewhere, it will not now be discussed further ; the data serve, however, to show how small a departure from the ideal formula is needed to emphasise the semi-metallic properties of such compounds.

The most important aspect of the subject that we have discussed is, however, its implications for chemical philosophy. The Berthollet-Proust controversy is recalled, and the status of the fundamental laws of chemical combination has to be reconsidered in the light of our wider knowledge. It seems that the law of constant proportions, which necessarily holds rigorously for compounds of discrete molecular constitution (e.g., gaseous compounds, and molecular liquids or solids), is a limiting law, to which solid compounds with atomic lattices approximate more or less closely ; with a few exceptions, indistinguishably closely. This conclusion, although revolutionary, seems inescapable. We have

certain parallels in the development of modern physics—for example, in the classical and quantum theories of radiation, and Bohr's correspondence principle ; or in the pragmatic viewpoint that confines the formulation of laws to quantities and properties that are, conceivably at least, experimentally observable. It is the task of the present generation of chemists to work out the implications of these conceptions, for the new outlook has to be built, sooner or later, into the fabric of the general theory and teaching of chemistry.

Bibliography.

Barrer, R. M., 1941. *Trans. Faraday Soc.*, **37**, 590.
Bernal, J. D., 1933. *Chem. Soc. Ann. Rep.*, **30**, 381.
Fritsch, O., 1935. *Ann. Physik.*, **22**, 375.
Grimm and Sommerfeld, 1926. *Z. Physik.*, **36**, 36.
Hägg, G., 1933. *Z. phys. Chem.*, B, **22**, 453.
Hägg, G., 1935. *Z. phys. Chem.*, B, **29**, 192.
Hedvall, J. A., 1931. *Angew. Chem.*, **44**, 781.
Jander, W., *et al.*, 1931*a*. *Z. anorg. allg. Chem.*, **199**, 165.
Jander, W., *et al.*, 1931*b*. *Z. anorg. allg. Chem.*, **199**, 306.
Jander, W., *et al.*, 1932. *Z. anorg. allg. Chem.*, **207**, 289.
Jander, W., 1934. *Angew. Chem.*, **47**, 235.
Jander, W., *et al.*, 1935. *Z. anorg. allg. Chem.*, **226**, 225.
Jette, E. R., and Foote, F., 1933. *J. Chem. Phys.*, **1**, 29.
Jost, W., 1937. Diffusion und chemische Reaktion in festen Stoffen. Steinkopf, Dresden.
Ketelaar, J. A. A., 1938. *Trans. Faraday Soc.*, **34**, 880.
Klemm, W., and Hass, W., 1934. *Z. anorg. allg. Chem.*, **219**, 82.
Koch, E., and Wagner, C., 1937. *Z. phys. Chem.*, B, **38**, 295.
Mott, N. F., and Gurney, R. W., 1940. Electronic Processes in Ionic Crystals. Oxford Univ. Press, Oxford.
Pauling, L., 1939. Nature of the Chemical Bond. Cornell Univ. Press, Ithaca.
Schottky, W., and Wagner, C., 1930. *Z. phys. Chem.*, B, **11**, 163.
Seitz, F., 1940. Modern Theory of Solids. McGraw Hill, New York. Chaps. I, II, IV, VIII, XIII, XV.
Strock, L. W., 1934. *Z. phys. Chem.*, B, **25**, 441.
Strock, L. W., 1936. *Z. phys. Chem.*, B, **31**, 132.
Tubandt, C., *et al.*, 1927. *Z. anorg. allg. Chem.*, **160**, 297.
Tubandt, C., *et al.*, 1931. *Z. anorg. allg. Chem.*, **197**, 225.
Tubandt, C., 1932. Handbuch exptl. Physik., Bd. XII, Teil 1.
Tubandt, C., *et al.*, 1933. *Z. Elektrochem.*, **39**, 227.
Tubandt, C., *et al.*, 1934. *Z. phys. Chem.*, B, **24**, 22.
Ubbelohde, A. R., and Oldham, J., 1940. *Proc. Roy. Soc.*, A, **176**, 50.
Wagner, C., 1933. *Z. phys. Chem.*, B, **21**, 25.
Wagner, C., 1934. *Z. phys. Chem.*, B, **25**, 71.
Wagner, C., 1936*a*. *Z. phys. Chem.*, B, **32**, 447.
Wagner, C., 1936*b*. *Angew. Chem.*, **49**, 735.
Wilson, A. H., 1931. *Proc. Roy. Soc.*, A, **133**, 458 ; **134**, 277.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales

April 1, 1942.

The Annual Meeting, being the five hundred and ninety-fourth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

Mr. D. P. Mellor, the President, was in the chair. Thirty-eight members and two visitors were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

A. B. WALKOM, D.Sc.

Vice-Presidents :

A. BOLLIGER, Ph.D., A.A.C.I.
IDA. A. BROWN, D.Sc.
H. PRIESTLEY, M.D., Ch.M., B.Sc.
H. S. HALCRO WARDLAW, D.Sc., F.A.C.I.

Honorary Secretaries :

PROF. A. P. ELKIN, M.A., Ph.D.
D. P. MELLOR, M.Sc.

Honorary Treasurer :

A. CLUNIES ROSS, B.Sc., F.C.A. (*Aust.*)

Members of Council :

G. H. BRIGGS, D.Sc., Ph.D., F.Inst.P.
J. A. DULHUNTY, B.Sc.
F. P. J. DWYER, M.Sc.
F. LIONS, B.Sc., Ph.D., A.I.C.
W. H. MAZE, M.Sc.
J. E. MILLS, M.Sc., Ph.D.
F. R. MORRISON, A.A.C.I., F.C.S.
R. S. NYHOLM, B.Sc.
G. D. OSBORNE, D.Sc., Ph.D.
H. H. THORNE, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S.
R. D. WATT, M.A., B.Sc.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Secretary, in the absence of the Honorary Treasurer, and on the motion of Professor A. P. Elkin, seconded by Mr. E. J. Kenny, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 28th FEBRUARY, 1942.

LIABILITIES.

1941. £		£ s. d.	£ s. d.	1942. £ s. d.
	Trust Funds—			
	Clarke Memorial Fund—			
	Balance as at 28th February, 1941 ..	1,779 19 0		
	Add Interest for year ended 28th February, 1942	71 4 0		
		£1,851 3 0		
	Less Expenses—1940 Lecture—			
	Printing £12 12 0			
	1941 Lecture and Medal—			
	Lecture Fee 26 5 0			
	Printing 20 18 9			
	Advertising 0 15 0			
	Engraving 0 11 0			
		61 1 9		
			1,790 1 3	
	Walter Burfitt Prize Fund—			
	Balance as at 28th February, 1941 ..	688 7 3		
	Add Interest for year ended 28th February, 1942	27 10 8		
		£715 17 11		
	Less Expenses in connection with 1941 Prize—			
	Fee for Prize £50 0 0			
	Printing 1 15 0			
	Engraving 0 6 6			
		52 1 6		
			663 16 5	
	Liversidge Bequest—			
	Balance as at 28th February, 1941 ..	686 1 4		
	Add Interest for year ended 28th February, 1942	27 8 10		
		£713 10 2		
	Less Expenses—Printing 1940 Lecture ..	13 6 6		
			700 3 8	
3,154				3,154 1 4
16	Subscriptions Paid in Advance	.. ..	..	14 14 0
124	Provisions for Unexpired Proportion of Life Membership Subscriptions			94 0 0
27,205	Accumulated Fund	.. ..	..	27,819 15 7
£30,499				£31,082 10 11

ASSETS.

1941. £		£ s. d.	1942. £ s. d.
	Cash at Bank and on Hand—		
	The Union Bank of Australia Ltd.	225 0 9	
	Commonwealth Savings Bank of Australia	52 19 5	
	Petty Cash	2 10 9	
101			280 10 11
	Bonds and Inscribed Stock—		
	Bonds (Face Value £1,000)	1,011 5 0	
	Stock (Face Value £7,860)	7,827 11 3	
8,439			8,838 16 3
	Science House Management Committee—		
14,650	Payments to date		14,650 0 0
	Sundry Debtors—		
	Subscriptions Unpaid	197 8 0	
—	*Less* Reserve	197 8 0	
6,800	Library		6,800 0 0
	Furniture—		
	Balance at 28th February, 1941	433 18 4	
	Add Additions	46 15 0	
		480 13 4	
	Less Depreciation written off	21 13 11	
434			458 19 5
	Pictures	41 11 11	
	Less Depreciation written off	2 1 7	
42			39 10 4
	Microscopes	18 9 2	
	Less Amount written off	18 9 2	
18			—
	Lantern	15 9 6	
	Less Depreciation written off	0 15 6	
15			14 14 0
£30,499			£31,082 10 11

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1942, as disclosed thereby. We have obtained certificates showing that the whole of the Bonds and Inscribed Stock are held by the Society's bankers for safe keeping.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 18th March, 1942.

(Sgd.) A. R. PENFOLD,
Hon. Treasurer.

REVENUE ACCOUNT FOR THE YEAR ENDED 28th FEBRUARY, 1942.

Year ended 28th Feb., 1941.			Year ended 18th February, 1942.	
£	£		£ s. d.	£ s. d.
	3	To Advertising	4 4 5	
	32	,, Cleaning	36 0 0	
	25	,, Depreciation	24 11 0	
	9	,, Electric Light and Gas	11 2 6	
	14	,, Insurance	14 13 5	
	40	,, Library Maintenance	36 7 3	
	55	,, Miscellaneous Expenses	63 3 10	
	284	,, Office Salaries and Audit Fees	292 2 0	
	16	,, Office Sundries and Stationery	28 13 0	
	115	,, Printing	163 19 3	
	362	,, Printing and Publishing Journal	452 16 8	
	5	,, Repairs	5 17 9	
	51	,, Stamps and Telegrams	55 8 10	
	19	,, Telephone	15 18 7	
		,, Annual Dinner—		
35		Expenses — £0 0 0		
29	6	*Less* Received — 0 0 0		
—			0 0 0	
	1,036			1,204 18 6
	443	,, Balance, being Net Revenue for the Year, transferred to Accumulated Fund		683 11 4
	£1,479			£1,888 9 10

Year ended 28th Feb., 1941.			Year ended 28th February, 1942.	
£	£		£ s. d.	£ s. d.
	531	By Members' Subscriptions		504 0 0
	400	,, Government Subsidy for years 1941 and 1942		800 0 0
275		,, Science House Receipts	325 0 0	
42		*Less* Rent Paid	42 7 2	
—	233			282 12 10
	99	,, Miscellaneous Receipts		74 1 4
307		,, Interest Received	323 19 2	
		Less—		
		Clarke Memorial Fund — £71 4 0		
		Walter Burfitt Prize Fund — 27 10 8		
123		Liversidge Bequest — 27 8 10		
—	184		126 3 6	
				197 15 8
	32	,, Proportion of Life Members' Subscriptions		30 0 0
	£1,479			£1,888 9 10

ACCUMULATED FUND ACCOUNT FOR THE YEAR ENDED 28th FEBRUARY, 1942.

1942—February 28—	£	s.	d.
To Arrears of Subscriptions, written off	50	8	10
,, Microscopes, written off	18	9	2
,, Balance Carried Down	27,819	15	7
	£27,888	13	7

1941—February 28—	£	s.	d.
By Balance from last Account	27,204	17	5
1942—February 28—			
By Amount transferred from Bad Debts Reserve Account	0	4	10
,, Net Revenue for the Year	683	11	4
	£27,888	13	7
1942—February 28—			
By Balance Brought Down	£27,819	15	7

The Annual Report of the Council (1941-42) was read, and on the motion of Professor A. P. Elkin, seconded by Dr. A. Bolliger, was adopted.

Report of the Council (Rule XXVI), 1941-42.

We regret to report that the Society has lost by death four members: Richard Thomas Baker (elected 1894), Leon Macintosh Ellis (1935), Edward George Noble (1891) and Carl Gustaf Sundstrom (1918).

The following fourteen members have resigned: R. F. Boan, W. Dudgeon, Miss L. Fraser, G. H. Godfrey, F. R. Hewitt, A. S. Hoskins, R. E. Jeffrey, W. S. McGowan, Mrs. G. Needham, C. Scott Waine, H. B. Mathews, C. H. Hoskins, R. D. Wilson and F. W. Booker.

The names of three members have been removed from the register.

Eleven ordinary members have been elected during the year, and the membership now stands at 294 ordinary and seven honorary members. The new members are Victor le Roy Alldis, Samuel Raymond Brown, Max Charles Cohen, David Parker Craig, Harold Theodore Clyde Howard, George Livingstone Melville, Matthew John Morrissey, Dansie Thomas Sawkins, Victoria Suvoroff, Thomas Baikie Swanson, and Irvine Armstrong Watson. Three of the Society's members are now on active service with the A.I.F., and one on home service with the R.A.A.F. Many of our members, both senior and junior, have been and still are engaged in important defence work, and the number of research papers has consequently declined. There has been considerable movement of our younger members to other States, also on national work.

Ten ordinary and two special meetings of Council have been held during the year beginning April 1st, 1941, at which the average attendance was 13.

Nine general meetings (including the Annual Meeting) were held, at which the average attendance was 36.

Twenty papers were accepted for publication during the year, and the following short talks were given:

"Fiji and the Fijians", by Arthur Capell, M.A., Ph.D.
"Mineral Resources of the Great Powers in Relation to the International Situation", by G. D. Osborne, D.Sc.
"A Scale of Magnitudes", by F. Lions, Ph.D.
"The Electron Microscope", by R. E. B. Makinson, Ph.D.
"Vitamin B_1—its Discovery and Importance in Nutrition and Disease Prevention", by A. Bolliger, Ph.D.
"The Sulphanilamide Drugs", by F. Lions, Ph.D.

The following exhibits were shown at meetings:

"Some Recent Developments in Plastics", by F. R. Morrison, A.A.C.I., F.C.S.
"A Fluorescent Chromatographic Column", by A. J. Tow, M.Sc.
"The Jelley-Leitz Refractometer", by G. D. Osborne, D.Sc.

By courtesy of the Rural Bank of N.S.W. films were shown and a commentary provided on "The Menace of Soil Erosion" and "The Red Terror" (bush fires).

Five Popular Science Lectures were given during the months June-October inclusive, and were well attended by the general public and by members of the Society.

June 19th.—" Some Aspects of Hydatid Disease in Australia ", by Professor H. Dew, M.B., B.S., F.R.C.S.
July 17th.—" The Modern Aeroplane ", by Professor A. V. Stephens, M.A.
August 21st.—" War and the Fisheries ", by H. Thompson, M.A., D.Sc.
September 18th.—" Weighing the Stars ", by R. van der R. Woolley, M.Sc., Ph.D.
October 16th.—" The Cow, the Chemist and Ourselves—The Nutrition of Farm Animals In Plenty and in Drought ", by E. G. Hallsworth, B.Sc., Ph.D. (London).

A Symposium was held, the subject chosen for discussion being " Light Metals ". The following were the speakers and subjects :

" Sources of Light Metals ", Professor L. A. Cotton.
" Manufacture of and Demand for the Light Metals ", Dr. J. E. Mills.
" Some Alloys of the Light Metals ", Miss V. Suvoroff.

The Annual Dinner was not held this year. This is consequent on the decision made last year to follow the precedent set during the 1914-1918 war, and not hold an annual dinner again during the present war.

The Clarke Memorial Lecture.—The Clarke Memorial Lecture was delivered by Mr. C. A. Sussmilch. The subject was " The Climate of Australia in Past Ages ".

The Clarke Memorial Medal.—The Clarke Memorial Medal for 1941 was awarded to Professor F. Wood Jones, F.R.S., formerly of the University of Melbourne, and now Professor of Anatomy in the University of Manchester. The medal was presented to Professor Wood Jones at the anniversary meeting of the Royal Society (London) held on December 1st, 1941.

The Walter Burfitt Prize.—The Walter Burfitt Prize was awarded to Frederick W. Whitehouse, D.Sc., Ph.D., Lecturer in Geology in the University of Queensland, for his work on the geology of Queensland.

Government Grant.—A grant of £400 was received by the Society from the Government of New South Wales.

Guide to Authors.—A committee was formed to revise and improve upon the existing leaflet of instructions to authors. The little brochure which resulted from the committee's work provides comprehensive instructions to authors of papers, and should prove most helpful both to the authors and to the editors of the volume.

Change in Format of Journal and Proceedings.—One outcome of war conditions and the consequent need for economy in printing, following the government regulations rationing paper, was the decision made, after careful inquiry and consideration, in late 1940 and early 1941, to alter the format of the Journal and Proceedings of the Society, enlarging it to a size of approximately $7\frac{1}{4} \times 9\frac{1}{4}$, the present size of the Linnean Society's journal. The change allows of economy in printing and paper, and of a more satisfactory arrangement of plates ; it also brings the Society's journal into line with other long established publications abroad, such as the Chemical Society of London, American Chemical Society, and Philosophical Magazine, all of which have been enlarged in recent years. The change began with the first part of Volume 75.

Revision of Rules.—The committee appointed early in 1941 has met on a number of occasions and continued with the thorough examination of the rules, which was begun in 1940. The results of the committee's work will be embodied in a report to be placed before a general meeting early in the year.

During 1941, for the first time in the history of the Society, a woman member was elected to the office of member of the Council, namely Dr. Ida A. Brown.

Professor T. G. Room, a member of the Council for several months of the year, was made a Fellow of the Royal Society (London).

The Library.—The Council accepted with regret the resignation of Professor Earl from the post of Honorary Librarian. Mr. W. H. Maze was appointed Honorary Librarian, in his place, and Dr. A. Bolliger was appointed Assistant Honorary Librarian.

Purchase of Periodicals and Binding.—The amount of £30 10s. 2d. has been expended on the purchase of periodicals during the year. A number of periodicals have been bound at a cost of £5 17s. The total cost of binding and purchase of periodicals amounted to £36 7s. 2d.

Exchanges.—The number of countries and societies exchanging publications with this Society has been further reduced since the last report was made, owing to the extension of the war zones.

The following countries have been removed from the exchange list since the war began : Austria, Czechoslovakia, Germany, Italy, Belgium, France, the Netherlands, Norway, Roumania, Jugoslavia, Finland, Hungary, Japan, Straits Settlements, Netherlands East Indies, Philippine Islands, Mandated Territory of New Guinea, and Sweden—the last four, because mail is being returned as " non-transmissible ". The number of societies with which we still exchange is 239 in the British Empire and abroad.

Accessions.—For the twelve months ended February 28th, the number of accessions entered in the catalogue was 2,563 parts of periodicals and 139 whole volumes.

Borrowers and Readers.—The readers visiting the library during the year numbered 35 : the number of books and periodicals borrowed by institutions, members and accredited readers has been 70. Among institutions which made use of the arrangement for inter-library borrowing were : The University of Sydney (Fisher Library, Chemistry School), University of Queensland, University of Adelaide, Sydney Technical College, Royal Society of Tasmania, the Council for Scientific and Industrial Research (McMaster Laboratory, Sydney, and Head Office, Melbourne), the Parliamentary Library, Canberra, the Commonwealth Solar Observatory, Mt. Stromlo, Canberra, and the British Medical Association, Sydney.

General.—Shelving has been erected at a cost of £39 10s. in the store-room, and the stock of volumes of Proceedings is now satisfactorily stored therein in an orderly manner. The librarians organised a working bee for the purpose and a general clearance of much unnecessary material was effected.

It was decided also to dispose of a number of old text-books in various sciences, in order to make room for the ever-growing number of periodicals. Some of these books have been given to university departments to which they will be of use.

Central Library.—A proposal to combine the libraries of the Royal Society, Linnean Society and Institution of Engineers was not approved of by the latter body. However, the Royal Society and Linnean Society have decided to attempt to make their libraries complementary.

A start has been made on this by compiling a list of periodicals which are duplicated in these libraries.

Recommendations.—It is recommended that the removal and storage of selected periodicals, which may be consulted in the Linnean Society library, be proceeded with. With the space made available by this and by the removal of the text-books the library will need to be rearranged. This will require the employment of a full-time librarian for a period of one or two months.

It is also recommended that the binding of periodicals be proceeded with at a faster rate than during 1941-1942.

D. P. MELLOR,
President.

The following donations were received : 540 parts of periodicals and 39 whole volumes.

The certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The certificate of a candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society : Jack Leslie Still.

The President announced that the Clarke Memorial Lecture for 1942 would be given by Mr. E. C. Andrews, the title of the lecture being " The Heroic Period of Geological Work in Australia ".

Election of Auditor.—On the motion of Professor A. P. Elkin, seconded by Mr. A. D. Ollé, Messrs. Horley & Horley were reappointed as the Society's auditors for the year 1942-43.

The President, Mr. D. P. Mellor, delivered his address, entitled " The Stereochemistry of Square Complexes ".

Mr. Mellor then installed Professor H. Priestley, M.D., Ch.M., B.Sc., as President for the year 1942-43. Professor Priestley expressed his appreciation of the honour conferred on him by the members.

Professor C. E. Fawsitt proposed a vote of thanks to the retiring President, Mr. D. P. Mellor, for his address, and on behalf of the members expressed appreciation of the work done for the Society by Mr. Mellor during his term of office. Mr. Mellor briefly replied.

The following papers were read by title only :

" Methæmoglobin Formation ", by J. W. Legge, B.Sc. (Communicated by Dr. M. R. Lemberg.)

" A Note on the Essential Oil of Eucalyptus Conglobata var. Anceps ", by P. A. Berry, M.Sc., and T. B. Swanson, M.Sc.

" Studies in Metamorphism and Assimilation in the Wellington District, N.S.W. Part II. The Dynamic and Contact Metamorphism of a Group of Ultrabasic Rocks ", by Elizabeth M. Basnett, M.Sc.

May 6, 1942.

The five hundred and ninety-fifth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 4.30 p.m.

The President, Professor H. Priestley, was in the chair. Nineteen members were present. The minutes of the previous meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member of the Society, namely John Conrad Jaeger, was read for the first time.

The certificate for a candidate for admission as an ordinary member of the Society was read for the second time. Owing to the fact that there were not sufficient members present to form a quorum, the ballot for election was deferred until the next meeting.

The following donations were received : 186 parts of periodicals and 13 whole volumes.

Notice of Motion.—Mr. A. D. Ollé gave notice of the following motion to be moved at the next meeting :

" That, for the duration of the war, a ballot for the election of new members shall be valid, provided that at least twelve members record their votes."

The following papers were read :

" The Tertiary Land Surface in Southern New England ", by A. H. Voisey, M.Sc.

" Spermatorrhœa in Marsupials with Special Reference to the Action of Sex Hormones on Spermatogenesis of Trichosurus Vulpecula ", by Adolph Bolliger, Ph.D.

" The Occurrence of Two Physiological Forms of Leptospermum Citratium (Challinor, Cheel and Penfold) as Determined by Chemical Analysis of the Essential Oils ", by A. R. Penfold, F.A.C.I., F.C.S., F. R. Morrison, A.A.C.I., F.C.S., and S. Smith-White, B.Sc.Agr.

June 3, 1942.

The five hundred and ninety-sixth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 6.30 p.m.

The President, Professor H. Priestley, was in the chair. Fifteen members were present. The minutes of the previous meeting were read and confirmed.

Owing to the fact that there were not enough members present to form a quorum, the ballot for the election of two members was postponed.

The President announced that the Clarke Memorial Medal for 1942 had been awarded to William Rowan Browne, D.Sc., Assistant-Professor of Geology in the University of Sydney, for his researches in geology and for the work he has done in correlating a large amount of material and preparing it for publication in the book on the geology of the Commonwealth, begun by the late Sir Edgeworth David.

Broadcast Talks.—It was announced that the following broadcast talks would be given this year in place of the Popular Science Lectures :

Tuesday, July 7th.—" Vitamins and the Loaf of Bread ", by Professor H. Priestley, M.D., Ch.M., B.Sc.

Tuesday, July 14th.—" Chemical Wonders : Glass from Coal—Rubber from Petroleum ", by A. R. Penfold, F.A.C.I., F.C.S.

Tuesday, July 21st.—" Minerals in Peace and War ", by G. D. Osborne, D.Sc.

Tuesday, July 28th.—" Chemical Harvest of the Sea ", by D. P. Mellor, M.Sc.

The following donations were received : 94 parts of periodicals and one whole number.

Notice of Motion.—As there were not enough members to form the necessary quorum, the motion of which Mr. Ollé had given notice was postponed.

The following paper was read :

" The Chemistry of Bivalent and Trivalent Rhodium. Part IV. Polynuclear Complexes of Rhodium and Tin with Tertiary Arsines ", by F. P Dwyer, M.Sc., and R. S. Nyholm, B.Sc.

A lecturette was given by Professor A. P. Elkin on " The Native Peoples of the Australian Territories ".

July 1, 1942.

The five hundred and ninety-seventh General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Professor H. Priestley, was in the chair. Forty-four members and nineteen visitors were present. The minutes of the previous meeting were read and confirmed.

Dr. J. L. Still, a new member, was welcomed by the President, and duly enrolled as a member.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : John Conrad Jaeger and Desmond J. Brown.

The President announced that the broadcast talks would be relayed from Station 2FC on National Network to all States.

The following donations were received : 118 parts of periodicals and two whole volumes.

Notice of Motion.—Mr. Challinor moved, on behalf of Mr. Ollé :

" That for the duration of the war a ballot for the election of new members shall be valid provided that at least twelve members record their votes."

The motion was seconded by Professor Elkin and carried.

An addition proposed by Mr. A. Maccoll, seconded by Mr. G. K. Hughes, namely, " and that a ballot be taken by a show of hands ", was ruled to be out of order.

Symposium.—A symposium on Rubber was held, and the following were the speakers and subjects :

Mr. D. H. Priestley, factory manager, Dunlop Rubber Co. (Aust.) : " Some important natural rubber sources."

Dr. F. Lions : " Some aspects of the chemistry of natural and synthetic rubber."

Mr. W. H. Maze : " Production and international control of rubber."

Mr. F. L. Milthorp : " Possible plant sources of rubber in Australia."

The following members and visitors took part in the discussion which followed the addresses : Private Moore, Mr. Lauder, Mr. Stuart Lucy, Mr. Miller, Dr. Harker and Mr. Millership.

Mr. Milthorp, Mr. Lions, Mr. Maze and Mr. D. H. Priestley replied to questions, and the President thanked those who had addressed the meeting.

August 5, 1942.

The five hundred and ninety-eighth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Professor H. Priestley, was in the chair. Thirty-three members were present. The minutes of the previous meeting were read and confirmed.

Dr. C. Anderson's resignation from the offices of Joint Honorary Secretary and Editor was announced, and was commented on by the President and Professor W. R. Browne.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time : Neville Allan Gibson and Raymond Norman Matthew Lyons.

The following donations were received : 120 parts of periodicals and seven whole volumes.

Motion from last Meeting.—Mr. Challinor, on behalf of Mr. Ollé, moved for the second time :

" That for the duration of the war, a ballot for the election of new members shall be valid, provided that at least twelve members record their votes."

The motion was seconded by Dr. A. Bolliger and carried.

Notice of Motion.—Mr. A. Maccoll and Mr. G. K. Hughes moved :

" (*a*) Rule VIII. That the 5th and 6th paragraphs shall read :

" ' The vote for admission shall take place by a show of hands, at the Ordinary General Meeting at which the certificate is appointed to be read the second time. Notwithstanding the above, any member shall have the right to demand a secret ballot. No election for new members shall be valid unless twelve members at least record their votes.

" ' At the election the assent of at least four-fifths of the members voting shall be requisite for the admission of the candidate.'

" (*b*) Rule L. That the following paragraph be added to Rule L :

" ' Any notice of motion to be moved at any Ordinary General Meeting must be in the hands of the Secretary before the Council Meeting immediately preceding the Ordinary General Meeting. The Secretary shall then cause such notices of motion to appear on the Agenda Paper of the Ordinary General Meeting.'

" ' This implies the following amendment to :

" Rule XXIII. ' That section (II) Rule XXIII be deleted, sections 12, 13, 14 to be renumbered 11, 12, 13.' "

After discussion the proposed alterations to these rules were referred back to the Council.

Proposed Alteration of Rules.—The Rules were dealt with as follows :

Rules I and II were passed.

Rule III was passed with one alteration, namely that the word " retiring " be replaced by " immediate past ", the rule to read :

Honorary Officers.

III. The other Officers of the Society shall consist of the President, who shall hold office for not more than one year continuously, but shall be eligible for re-election after the lapse of one year ; four Vice-Presidents, an Honorary Treasurer, and two Honorary Secretaries, who, with ten other members, shall constitute the Council for the management of the affairs of the Society.

The President, Honorary Secretaries and Honorary Treasurer and immediate past President shall constitute the Executive Committee of the Society.

Rule IV, with one alteration, namely, that the words " by postal ballot to be declared " be omitted. The Rule now reads :

Election of Honorary Officers and Council.

IV. The President, Vice-Presidents, Honorary Secretaries, Honorary Treasurer, and the *ten* other members of Council, shall be elected annually at the first General Meeting in the month of April, hereinafter called the Annual General Meeting.

Rule V was dealt with as follows : Paragraph 1 was passed. On the motion of Dr. Lions, seconded by Mr. Dwyer, paragraph 2 to read :

Any member of the Society not disqualified by Rules XVI, XVII or XVIII, may be nominated for the position of President, Vice-President, Honorary Treasurer, Honorary Secretary, or Member of the Council, provided that his candidature shall have been notified to the Honorary Secretaries under the hands of two qualified voters—such notification being countersigned by the nominee—not later than the first Wednesday in March, at 5 p.m., and provided also that no member shall be eligible for election to the position of Member of the Council if he shall have served on the Council for any four of the preceding five years.

On the motion of Dr. Lions, seconded by Mr. Maccoll, paragraph 3 to read :

A complete list showing the names arranged in alphabetical order, together with their nominators, of those correctly nominated for election to the Council, shall be posted to each financial member of the Society not less than twenty-one days before the day appointed for the Annual General Meeting.

On the motion of Dr. Lions, seconded by Mr. Dwyer, a new paragraph 4 was introduced, to read :

Any member of the Society not disqualified by Rules XVI, XVII, or XVIII may make written application to the Honorary Secretaries of the Society for an absentee vote. Such application must be made within the fortnight preceding the Annual General Meeting and must be in the hands of the Honorary Secretaries not later than noon on the Tuesday preceding the Annual General Meeting. The absentee voter's completed ballot paper must have been returned to the Honorary Secretaries by not later than 5 p.m. on the day of the Annual General Meeting.

Paragraphs 4 and 5 of the draft rules now become numbers 5 and 6 of Rule V, and were passed :

The name of each member voting shall be checked by two scrutineers appointed by the Council at its meeting next before the Annual General Meeting.

No ballot for the election of members of Council shall be valid unless twenty members at least shall record their votes.

Rule VI was passed.

Rule VIII was referred back to the Council.

Rule IX was amended and now reads :

Subscriptions.

IX. The Annual Subscription shall be two guineas, payable in advance, but members who are under twenty-eight years of age shall be required to pay only one guinea yearly.

The amount of twenty-five guineas may be paid at any one time by a financial member as a life composition for the ordinary annual payment.

A member who has paid the annual subscription for thirty-five years shall become a life member without payment of further subscriptions.

The Council shall have the power to suspend from membership temporarily, for a period not exceeding two years, any member who may in writing make such application to it on the grounds of financial difficulties.

Rule XI was passed.

Rule XIV was passed.

Rule XV, after the deletion of the words " as in advance for the following year ", was passed, and now reads :

XV. Persons elected on or after the first day of October in any year shall pay half the appropriate annual subscription for that financial year.

Rule XVII was amended by the transfer of paragraph 3 to become paragraph 3 of Rule XVIII. Rule XVII now reads :

Subscriptions in Arrears.

XVII. Members who have not paid their subscriptions for the current financial year, on or before the 30th day of April, shall be informed of the fact by the Honorary Treasurer. Rule XVIII, with the addition of paragraph 3 from Rule XVII, now reads :

XVIII. A member is deemed to be in arrears if his subscription for the previous financial year has not been paid.

Any member in arrears shall cease to receive the Society's publications, and shall not be entitled to any of the privileges of the Society until such arrears are paid.

The name of any member who shall be two years in arrears with his subscription may be erased from the list of members, but such member may be readmitted on giving a satisfactory explanation to the Council, and on payment of such arrears as the Council may determine.

The following papers were read :

" Coordination Complexes of Rhodous Halides with Dialkyl Arsines ", by F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc.

" The Effect of Gonadotropin Obtained from Human Pregnancy Urine on the Pouch of Trichosurus Vulpecula ", by A. Bolliger, Ph.D.

" On Contact Transformations Associated with the Symplectic Group ", by H. Schwerdtfeger. (Communicated by Prof. H. S. Carslaw.)

" The Devonian Rugose Corals of the Tamworth District, N.S.W.", by Dorothy Hill, Ph.D., D.Sc.

" The Tamworth Series (Lower and Middle Devonian), Near Attunga, N.S.W.", by Ida A. Brown, D.Sc.

September 2, 1942.

The five hundred and ninety-ninth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Professor H. Priestley, was in the chair. Twenty-four members and one visitor were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time : Gordon Roy Williams and Arthur S. Lippmann.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Neville Allan Gibson and Raymond Norman Matthew Lyons.

The following donations were received : 86 parts of periodicals and seven whole volumes.

Correspondence.—A letter from His Excellency the Governor-General, Lord Gowrie, acknowledging a letter of sympathy on the death of H.R.H. the Duke of Kent, and stating that the message was being sent by mail to London.

Notices of Motion.—Dr. Bolliger moved :

" That notwithstanding Rule IX, the subscription be one guinea for the duration of the war."

Mr. Maccoll moved :

" That notwithstanding Rule IX the subscription be reduced by 50 per cent. for the duration of the war."

The President moved :

" That notwithstanding Rule IX, the subscription be one and a half guineas for those 28 years of age and over, and one guinea for those under 28 years of age."

All three motions were postponed until a later date, owing to the lack of the necessary quorum of 25.

Proposed Alterations to Rules.—The proposed alterations to the Rules, as circulated in printed form, could not be put to the vote owing to the lack of the necessary quorum of 25 members, and were postponed until the next meeting.

The following papers were read :

" Middle Palaeozoic Rugose Corals from the Wellington District, N.S.W.", by Dorothy Hill, Ph.D., D.Sc.

" Some Thermochemical Properties of the Torbanite of the Glen Davis Deposit ", by R. F. Cane, M.Sc.

Notice of Motion.—Mr. Maccoll gave notice that he would move at the next meeting the adoption of the Rules as circulated for the September meeting.

October 7, 1942.

Six hundredth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Professor H. Priestley, was in the chair. Forty-nine members and eight visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Arthur S. Lippmann and Gordon Roy Williams.

The following donations were received : 66 parts of periodicals.

Motions from last Meeting.—Consideration of the three motions from last meeting was again postponed.

Proposed Alteration to Rules.—Mr. Maccoll withdrew his motion for the adoption of the Rules as circulated for the September meeting.

Mr. Maccoll also withdrew his motion that another paragraph be added to Rule L.

The following papers were read by title only :

"Moving Sources of Heat and the Temperature at Sliding Contacts", by J. C. Jaeger, M.A., D.Sc.

"A Method for the Estimation of Vegetable Material in Scoured Wool", by M. Lipson, B.Sc., A.A.C.I.

Clarke Memorial Medal.—The President, after a short address on the Rev. W. B. Clarke and the purpose of the Medal, presented the medal to Dr. W. R. Browne, who briefly expressed his thanks.

Tercentenary of Galileo and Newton.—To mark the tercentenary of the death of Galileo and the birth of Newton, an address was given by Professor O. U. Vonwiller, entitled "Galileo and Newton : Their Times and Ours".

November 4, 1942.

The six hundred and first General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Professor H. Priestley, was in the chair. Twenty-eight members and two visitors were present. The minutes of the previous meeting were read and confirmed.

The following donations were received : 120 parts of periodicals and five whole volumes.

Notices of Motions from last Meeting.—Mr. Maccoll withdrew his motion for the reduction of subscriptions by 50 per cent. for the duration of the war.

Dr. Bolliger moved :

"That the annual subscription be One Guinea per annum for the duration of the war."

After discussion the motion was lost by 13 votes to 11.

Alteration of Rules.—Mr. Maccoll moved the adoption of the rules as circulated for the September meeting, and the rules were dealt with as follows :

All the altered rules were adopted with the exception of Rule V. An amendment was moved by Professor Elkin, seconded by Mr. Mellor, that the first sentence of paragraph 4, Rule V, as printed and circulated, be altered to read :

"Provision shall be made for any member of the Society to record an absentee vote provided that such member is not disqualified by Rules XVI, XVII, or XVIII, and makes written application to the Honorary Secretary for a ballot paper for this purpose."

This was put as a substantive motion and carried, 27 voting.

Rule V now reads :

V. It shall be the duty of the Council each year to prepare a list containing the names of members whom they recommend for election to the respective offices of President, Vice-Presidents, Honorary Secretaries, and Honorary Treasurer, together with the names of *ten* other members whom they recommend for election as ordinary members of Council.

Any member of the Society not disqualified by Rules XVI, XVII or XVIII, may be nominated for the position of President, Vice-President, Honorary Treasurer, Honorary Secretary, or Member of the Council, provided that his candidature shall have been notified to the Honorary Secretaries under the hands of two qualified voters—such notification being countersigned by the nominee—not later than the first Wednesday in March, at 5 p.m., and provided also that no member shall be eligible for election to any office on the Council other than that of President, Vice-President, Honorary Treasurer or Honorary Secretary, if he shall have served on the Council for any four of the preceding five years.

A complete list showing the names arranged in alphabetical order, together with their nominators, of those correctly nominated for election to the Council, shall be posted to each financial member of the Society not less than twenty-one days before the day appointed for the Annual General Meeting.

Provision shall be made for any member of the Society to record an absentee vote provided that such member is not disqualified by Rule XVI, XVII, or XVIII, and makes written application to the Honorary Secretary for a ballot paper for this purpose. Such application must be made within the fortnight preceding the Annual General Meeting and must be in the hands of the Honorary Secretaries not later than noon on the Tuesday preceding the Annual General Meeting. The absentee voter's completed ballot paper must have been returned to the Honorary Secretaries by not later than 5 p.m. on the day of the Annual General Meeting.

The name of each member voting shall be checked by two Scrutineers appointed by the Council at its meeting next before the Annual General Meeting.

No ballot for the election of members of Council shall be valid unless twenty members at least shall record their votes.

Rules VI, IX, XIV, XV, XVII and XVIII. The adoption of these rules was moved by Mr. Maccoll, seconded by Mr. Dwyer, and carried, 28 voting.

Rules VIII, XIX, XX, XXIII, XXIV, XXVII, XXVIII, XXIX and XXX. The adoption of these rules was moved by the President, Professor H. Priestley, seconded by the Honorary Secretary, Professor Elkin, and carried, 28 voting.

Rules XXXI, XXXII, XXXIII, XXXV, XXXVIII, XLI, XLIV and XLIX. The adoption of these rules was moved by the President, Professor H. Priestley, seconded by the Hon. Secretary, Professor Elkin, and carried, 27 voting.

Rule L. Mr. Maccoll accepted Professor Elkin's amendment in place of his own, of which notice had been given. The amendment, namely that the following be added to Rule L :

> " Provided also that notice of motion of such alteration of, or addition to, the Rules be given in the notice paper summoning the ordinary General Meeting immediately preceding the General Meeting at which the motion is to be moved for the first time "

became a substantive motion, on the motion of Professor Elkin, seconded by Mr. Maccoll, and was carried, 27 voting.

The following paper was presented by Mr. E. Cheel :

" A Revision of Certain Species of Leptospermeae."

A discussion took place on Mr. Lipson's paper on " A Method for the Estimation of Vegetable Material in Scoured Wool ", which had been read by title at the previous meeting.

An exhibit was shown by Mr. J. A. Dulhunty of products from solvent extraction of torbanite (oil shale).

December 2, 1942.

The six hundred and second General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Professor H. Priestley, was in the chair. Fifty-five members were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Mr. Gerald H. Halligan, a member since 1880.

The certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The following donations were received : 84 parts of periodicals and five whole volumes.

Alteration of Rules.—The President moved the confirmation of Rules I to IV and VI to L. The motion was seconded by Professor Elkin, and carried unanimously.

The President moved the confirmation of the alteration to Rule V, as agreed to at the previous meeting. This was seconded by Dr. Murphy. Dr. W. R. Browne moved an amendment, seconded by Mr. Maze, namely that all the words after " 5 p.m." be omitted, and instead the rule to read " and provided also that three new members of Council be elected each year ".

After discussion the amendment was ruled out of order. Mr. A. E. Stephen moved that the motion be now put. Dr. Murphy seconded the motion, but on the motion of Mr. R. W. Challinor, seconded by Dr. G. Harker, it was agreed that Dr. Browne be heard regarding the second point of his objection to Rule V. This concerned the making of an application for an absentee vote. Dr. Lions spoke supporting the present alteration, and Professor Cotton favoured a general postal vote.

Before the motion was put, the President explained that those agreeing with Professor Browne's argument, should vote against the motion, the consideration of which would then be postponed until next year.

The motion was then put, and carried by 27 votes to 14.

The following papers were read :

" Upper Ordovician Graptolite Horizons in the Yass-Jerrawa District, N.S.W.", by Kathleen Sherrard.

" Physiography of the Wellington District, N.S.W.", by Margaret J. Colditz.

" Permian Bryozoa of Eastern Australia ", Part III, by Joan M. Crockford.

" The Action of Solvents on Torbanite and the Nature of Extracted Products ", by J. A. Dulhunty.

" Progressive Rates of Tax in Australia ", Part II, by Professor H. S. Carslaw.

" The Chemistry of Bivalent and Trivalent Rhodium ", Part VI, by F. P. Dwyer and R. S. Nyholm.

" A Note on the Magnetic Behaviour of Potassium Cyano-nickelite ", by D. P. Mellor and D. P. Craig.

" Co-ordination Compounds Derived from Nicotinylacetone ", by F. Lions, B. S. Morris and E. Ritchie.

" Functional Relations between Scrotum and Pouch and the Experimental Production of a Pouch-like Structure in the Male of *Trichosurus vulpecula* ", by A. Bolliger.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Dr. W. R. Browne.

Honorary Secretary : Mr. R. O. Chalmers.

Eight meetings were held during the year, the average attendance being fourteen members and two visitors.

1942.

April 17th.—Address by Dr. G. D. Osborne, " Mount Egmont ".

May 15th.—Notes and Exhibits : By Mr. Chalmers : (*a*) (i) On behalf of Dr. Walkom : Leaves and sporangia of *Isoctites* from Gingin, Western Australia ; (ii) Large *Gangamopteris* from the Permian at Rylstone, N.S.W. ; (iii) *Microphyllopteris gleichenioides* from the Narrabeen Series at Newport, collected by Mr. O. Le M. Knight ; (*b*) Barite and picrolite from Dundas Quarry. By Mr. Dulhunty : Note on the classification of torbanites by plotting percentage of volatile constituents against the expansion at 300° C. By Mr. Lambeth : (*a*) Crystallised magnetite from Broula Range, near Cowra ; (*b*) Intergrowth between quartz and magnetite from the same locality. By Mr. Waterhouse : (*a*) Pectolite from Prospect ; (*b*) Basalt from the Hornsby breccia ; (*c*) Banded and faulted ore from Mount Isa. By Miss Colditz : Physiographic notes on the Wellington District. By Dr. Browne : Note on the physiography of the Snowy River, in the Jindabyne and Dalgety Districts.

June 19th.—Address by Dr. W. R. Browne, " Metallogenesis, Intrusion and Diastrophism in Eastern Australia ".

July 17th.—Address by Prof. L. A. Cotton, " Some Modern Conceptions of the Constitution of the Earth's Interior ".

August 14th.—Address by Dr. Ida A. Brown, " Some Recent Advances in Australian Palæozoic Stratigraphy ".

September 18th.—Address by Mr. J. Hanson-Lowe, sometime Lecturer in Geography, University of London, " The Analysis of Stream and other Profiles ".

October 16th.—Exhibit by Mr. Dulhunty : Specimen of tertiary coal from a seam beneath basalt at Wambrook Creek, 12 miles N.W. of Cooma, N.S.W. Discussion on the address given by Dr. W. R. Browne at the meeting of June 19th.

November 20th.—Notes and Exhibits : By Dr. Joplin : Siliceous graptolite-bearing slates, which may owe their high silica content not to subsequent silicification but to the peculiar conditions existing in the land-locked sea where the graptolites lived. By Mr. Voisey : An account was given of various maps that may be useful for geological work. By Mr. Dulhunty : Physiographical notes on the respective heads of rejuvenation of the Wolgan and Cox's Rivers. By Professor Cotton : Fossil bloodwood tree from the floor of Sydney Harbour. By Mr. T. Hodge-Smith : Exhibit of photographs of three of the fragments of the No. 1 Forest Vale aerolite, and the No. 2 stone itself. By Mrs. Sherrard : Graptolites from the Yass district. By Miss Quodling : Apparatus for producing interference figures and a note on the physical properties of the true and brittle micas in terms of atomic structure. By Mr. Chalmers : Permian fossil insect wings from Pincombe's outcrop between Belmont and Warner's Bay, N.S.W.

INDEX.

A

Page.

Abstract of Proceedings xxi
Section of Geology xxxiv
Action of Solvents on Torbanite and the Nature of Extracted Products .. 268
Alteration of Rules xxix
Anderson, J. S.—
Liversidge Research Lectures—
The Chemistry of the Earth 329
The Imperfect Crystal 345
Andrews, E. C.—
The Heroic Period of Geological Work in Australia (Clarke Memorial Lecture) 96
Annual Report and Balance Sheet .. xxii
Arsines, Dialkyl, Coordination Complexes of Rhodous Halides with, (Chemistry of Bivalent and Trivalent Rhodium) 133
Arsines, Tertiary, Polynuclear Complexes of Rhodium and Tin with, (Chemistry of Bivalent and Trivalent Rhodium) 129
Authors, Notice to v
Awards of—
Clarke Memorial Medal .. xviii
Liversidge Research Lectureship .. xx
Society's Medal and Money Prize .. xix
Walter Burfitt Prize xx

B

Balance Sheet xxii
Ballot for Election of Members, Rule *re*, during the War xxix
Basnett, Elizabeth M.—
Studies in Metamorphism and Assimilation in the Wellington District, N.S.W. II. The Dynamic and Contact Metamorphism of a Group of Ultrabasic Rocks 55
Bequest, Form of v
Berry, P. A.—See Swanson, T. B. .. 53
Bolliger, A.—
The Effect of Gonadotropin obtained from Human Pregnancy Urine on the Pouch of *Trichosurus vulpecula* .. 137
Functional Relations between Scrotum and Pouch and the Experimental Production of a Pouch-like Structure in the Male of *Trichosurus vulpecula* 283
Spermatorrhœa in Marsupials, with Special Reference to the Action of Sex Hormones on Spermatogenesis of *Trichosurus vulpecula* 86
Broadcast Talks xxviii

Page.

Brown, Ida A.—
The Tamworth Series (Lower and Middle Devonian), near Attunga, N.S.W. 165
Bryozoa, Permian, from Eastern N.S.W. Pt. III 258
Burfitt Prize xx

C

Cane, R. F.—
Some Thermochemical Properties of the Torbanite of the Glen Davis Deposit 190
Carslaw, H. S.—
Progressive Rates of Tax in Australia. Part II 304
Central Library, Proposals for .. xxvii
Cheel, E.—
A Revision of Certain Species of Leptospermeæ 229
Chemistry of Bivalent and Trivalent Rhodium. Part IV. Polynuclear Complexes of Rhodium and Tin with Tertiary Arsines 129
Chemistry of Bivalent and Trivalent Rhodium. Part V. Coordination Complexes of Rhodous Halides with Dialkyl Arsines 133
Chemistry of Bivalent and Trivalent Rhodium. Part VI. Pyridine Complexes of Rhodous Halides .. 275
Chemistry of the Earth (Liversidge Research Lecture) 329
Clarke Memorial Fund xviii
Clarke Memorial Lecture xviii, xxvii, 96
Clarke Memorial Medal xviii
Award to W. R. Browne .. xxxii
Colditz, Margaret J.—
Physiography of the Wellington District 235
Contact Transformations Associated with the Symplectic Group 177
Contents iii
Co-ordination Compounds Derived from Nicotinylacetone 294
Corals, Devonian Rugose, of the Tamworth District, N.S.W. 142
Corals, Middle Palæozoic Rugose, from the Wellington District, N.S.W. .. 182
Council, Report of the xxv
Craig, D. P.—See Mellor, D. P. 281
Crockford, Joan M.—
Permian Bryozoa of Eastern Australia 258
Crystal, The Imperfect (Liversidge Research Lecture) 345
Cyanonickelite, Magnetic Behaviour of Potassium 281

D

Page.
Devonian (Lower and Middle), The Tamworth Series, near Attunga, N.S.W. 165
Devonian Rugose Corals of the Tamworth District, N.S.W. 142
Dialkyl Arsines, Co-ordination Complexes of Rhodous Halides with 133
Dwyer, F. P., and Nyholm, R. S.—
The Chemistry of Bivalent and Trivalent Rhodium. Part IV. Polynuclear Complexes of Rhodium and Tin with Tertiary Arsines.. .. 129
The Chemistry of Bivalent and Trivalent Rhodium. Part V. Co-ordination Complexes of Rhodous Halides with Dialkyl Arsines .. 133
The Chemistry of Bivalent and Trivalent Rhodium. Part VI. Pyridine Complexes of Rhodous Halides .. 275
Dulhunty, J. A.—
The Action of Solvents on Torbanite and the Nature of Extracted Products 268
Dynamic and Contact Metamorphism of a Group of Ultrabasic Rocks (Metamorphism and Assimilation in the Wellington District, N.S.W.). Part II 55

E

Effect of Gonadotropin obtained from Human Pregnancy Urine on the Pouch of *Trichosurus vulpecula* .. 86
Essential Oil of *Eucalyptus conglobata* var. *anceps*, A Note on 53
Essential Oils. The Occurrence of Two Physiological Forms of *Leptospermum citratum* (Challinor, Cheel and Penfold) as determined by Chemical Analysis of the 93
Eucalyptus conglobata var. *anceps*, A Note on the Essential Oil of 53
Exchanges xxvi
Exhibits—
Products from Solvent Extraction of Torbanite (Oil Shale) .. xxxiii

F

Functional Relations between Scrotum and Pouch, and the Experimental Production of a Pouch-like Structure in the Male of *Trichosurus vulpecula* 283

G

Galileo and Newton—Their Times and Ours (Tercentenary Address) .. 316
Geological Work in Australia, the Heroid Period of 96
Page.
Glen Davis Deposit, N.S.W., Some Thermochemical Properties of the Torbanite of 190
Gonadotropin obtained from Human Pregnancy Urine, the Effect of, on the Pouch of *Trichosurus vulpecula* 137
Government Grant xxvi
Graptolite Horizons, Upper Ordovician, in Yass-Jerrawa District, N.S.W... 252
Guide to Authors xxvi

H

Heat, Moving Sources of, and the Temperature at Sliding Contacts.. 203
Heroic Period of Geological Work in Australia (Clarke Memorial Lecture) 96
Hill, Dorothy—
The Devonian Rugose Corals of the Tamworth District, N.S.W. .. 142
Middle Palæozoic Rugose Corals from the Wellington District, N.S.W... 182
Hormones, Sex, the Action of, on Spermatogenesis of *Trichosurus vulpecula* 86

I

Imperfect Crystal, The 345

J

Jaeger, J. C.—
Moving Sources of Heat and the Temperature at Sliding Contacts.. 203

L

Lecturette—
The Native Peoples of the Australian Territories xxviii
Legge, J. W.—
Methæmoglobin Formation 47
Leptospermum citratum (Challinor, Cheel and Penfold), the Occurrence of Two Physiological Forms of, as Determined by Chemical Analysis of the Essential Oils 93
Leptospermeæ, A Revision of Certain Species of 229
Library xxvi
Proposal for Central .. xxvii
Lions, F., Morris, B. S., and Ritchie, E.—
Co-ordination Compounds Derived from Nicotinylacetone 294
Lipson, M.—
A Method for the Estimation of Vegetable Material in Scoured Wool 225
List of Members ix
Liversidge Research Lectures—
The Chemistry of the Earth .. 329
The Imperfect Crystal 345

M

Page.
Magnetic Behaviour of Cyanonickelite 281
Marsupials, Spermatorrhœa in, with Special Reference to the Action of Sex Hormones on Spermatogenesis of *Trichosurus vulpecula* 86
Mellor, D. P.—
Presidential Address, The Stereochemistry of Square Complexes .. 7
Mellor, D. P., and Craig, D. P.—
A Note on the Magnetic Behaviour of Potassium Cyanonickelite 281
Members, List of ix
Metamorphism and Assimilation in the Wellington District, N.S.W., Studies in. Part II. The Dynamic and Contact Metamorphism of a Group of Ultrabasic Rocks 55
Methæmoglobin Formation 47
Method for the Estimation of Vegetable Material in Scoured Wool .. 225
Middle Palæozoic Corals from the Wellington District, N.S.W. 182
Morris, B. S.—See Lions, F. 294
Moving Sources of Heat and the Temperature at Sliding Contacts 203

N

Newton Tercentenary.—See Galileo .. 316
Nicotinylacetone, Co-ordination Compounds Derived from 294
Nyholm, R. S.—See F. P. Dwyer 129, 133, 275

O

Obituaries .. .. 5, xvii
Occurrence of Two Physiological Forms of *Leptospermum citratum* (Challinor, Cheel and Penfold), as Determined by Chemical Analysis of the Essential Oils 93
Officers for 1942-1943 vii
Ordovician (Upper), Graptolite Horizons in, Yass-Jerrawa District, N.S.W... 252

P

Palæozoic (Middle) Rugose Corals from the Wellington District, N.S.W... 182
Penfold, A. R., Morrison, F. R., and Smith-White, S.—
The Occurrence of Two Physiological Forms of *Leptospermum citratum* (Challinor, Cheel and Penfold) as Determined by Chemical Analysis of the Essential Oils 93
Permian Bryozoa from Eastern New South Wales 258
Physiography of the Wellington District 235
Potassium Cyanonickelite, A Note on the Magnetic Behaviour of .. 281
Pouch-like Structure, Experimental Production of, in the Male of *Trichosurus vulpecula* 283
Presidential Address by D. P. Mellor, The Stereochemistry of Square Complexes 7
Progressive Rates of Tax in Australia. Part II 304
Pyridine Complexes of Rhodous Halides 275

R

Report of the Council, 1941-1942 .. xxv
Revenue Account xxiv
Revision of Certain Species of Leptospermeæ 229
Rhodium, The Chemistry of Bivalent and Trivalent .. 129, 133, 275
Ritchie, E.—See Lions, F. 294
Rubber, Symposium on .. xxiv
Rules, Alteration of .. xxiv, xxx-xxxiii

S

Schwerdtfeger, H.—
On Contact Transformations Associated with the Symplectic Group 177
Scoured Wool, A Method for the Estimation of Vegetable Matter in 225
Sherrard, Kathleen—
Upper Ordovician, Graptolite Horizons in Yass-Jerrawa District, N.S.W... 252
Smith-White, S.—See Penfold, A. R. 93
Society's Medal and Money Prize .. xix
Some Thermochemical Properties of the Torbanite of the Glen Davis Deposit 190
Spermatorrhœa in Marsupials, with Special Reference to the Action of Sex Hormones on Spermatogenesis of *Trichosurus vulpecula* 86
Stereochemistry of Square Complexes, The 7
Studies in Metamorphism and Assimilation in the Wellington District, N.S.W. 56
Swanson, T. B., and Berry, P. A.—
A Note on the Essential Oil of *Eucalyptus conglobata* var. *anceps*.. 53
Symplectic Group, On Contact Transformations Associated with the .. 177
Symposium on Rubber xxix

T

Tamworth District, Devonian Rugose Corals of 142
Tamworth Series (Lower and Middle Devonian) near Attunga, N.S.W... 129
Tax, Progressive Rates of, in Australia.. 304
Tertiary Arsines, Polynuclear Complexes of Rhodium and Tin with, Chemistry of Bivalent and Trivalent Rhodium 129

Page.

Torbanite of Glen Davis District, N.S.W., Some Thermochemical Properties of.. 190

Torbanite, the Action of Solvents on, and the Nature of Extracted Products 268

Trichosurus vulpecula, Effect of Gonadotropin obtained from Human Pregnancy Urine on the Pouch of.. 137

Trichosurus vulpecula, Experimental Production of a Pouch-like Structure in the Male 283

Trichosurus vulpecula, Spermatorrhœa in Marsupials, with Special Reference to the Action of Sex Hormones on Spermatogenesis of 86

U

Upper Ordovician Graptolite Horizons in Yass-Jerrawa District, N.S.W... 252

V

Page.

Voisey, A. H.—
Tertiary Land Surface in Southern New England 82

Vonwiller, O. U.—
Tercentenary of Galileo and Newton—Address: Galileo and Newton—Their Times and Ours 316

W

Walter Burfitt Prize xx
Award to F. W. Whitehouse xxvi

Wellington District, Physiography of.. 235

Wellington District, Middle Palæozoic Corals from 182

Wool, Scoured, A Method for the Estimation of Vegetable Material in 225

Y

Yass-Jerrawa District, N.S.W., Upper Ordovician Graptolite Horizons in.. 252

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